ISOTOPIC STUDIES IN THE ELECTRONIC SPECTRA OF SeO, SeN AND Te$_2$ MOLECULES

BY

KOTA VENKATA SUBBARAM

DEPARTMENT OF PHYSICS

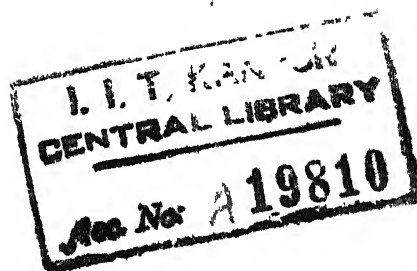## INDIAN INSTITUTE OF TECHNOLOGY KANPUR

MARCH, 1969

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A Thesis Submitted

in partial fulfilment of the requirements
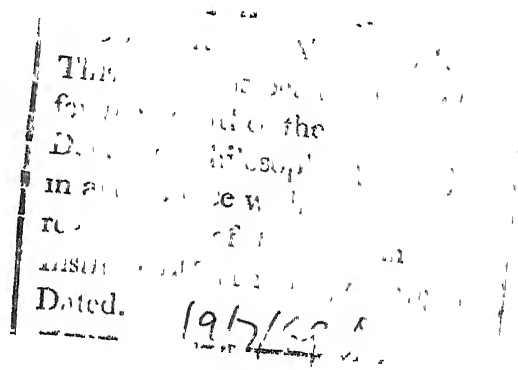
for the Degree of

DOCTOR OF PHILOSOPHY

by

KOTA VENKATA SUBBARAM

to the

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

March,1969

PREFACE

The use of enriched isotopes in the study of molecular spectra has become one of the most important means to arrive at definite conclusions about the emitter involved and the molecular parameters. By using separated isotopes, the spectra will become simpler avoiding the overlapping from the other abundant species in a natural sample. The vibrational and rotational analyses could be confirmed from isotopic studies. It is possible to say with certainity whether or not a particular atom is one of the constituents in the molecule under study.

An investigation of molecular spectra of Group VI elements and intercombination molecules belonging to the same group is interesting because of the transition of coupling of angular momenta from Hund's case(b) approximation to Hund's case(c), as one moves down the group from O_2 and S_2 to Se_2. While the molecules O_2 and SO belong strictly to Hund's case(b), it is known that TeO molecule goes over to Hund's case(c) SeO forming an intermediate case. Also, any study involving Se and Te should make use of separated isotopes, as both of them in their natural form have several isotopes of appreciable abundance.

The thesis mainly describes the work done by the author on SeO, SeN and Te_2 molecules making use of enriched isotopes of Se and Te.

A high vacuum system was constructed in the laboratory with the help of which sealed quartz discharge tubes for emission work were prepared using very little amounts of samples. This was done in a similar manner to that described by Tomkins and Fred (1957. J.Opt.Soc.Am., **47**, 1057). Attempts were made to excite new molecules with combinations of simple gases and selenium. Before a trial was made on the excitation of a new molecule, the technique of sealing was tried on the combination of Se (natural sample) and oxygen. The sealed tube was excited by a microwave oscillator and the resulting emission corresponded to the known bands of SeO in the near ultra-violet region. It has been shown by Barrow and Deutsch (1963. Proc.Phys.Soc. (London), **82**, 548) that this band system is due to a $^{3}\Sigma^{-} - {}^{3}\Sigma^{-}$ transition, with both the states belonging to Hund's case(b) with large ~~value~~λ value (hence it splits up into two sub-systems F_1-F_1 and $F_{2,3}-F_{2,3}$). A clos·er study of the observed spectrum in the present investigation revealed that the second sub-band in the $v'=2$ progression is perturbed by about $28cm^{-1}$. With the availability of enriched isotopes of selenium and the success of the sealing technique employed, it was possible to confirm the perturbation of $v'=2$ in the second subband of SeO, by the expected isotopic shifts. Some of the extra bands observed in the same region were assigned to cross-transitions of the type $F_{2,3}-F_1$ or $1 - 0^+$ in Hund's case(c) approximation. Chapter I(A) gives the details on the perturbation and a discussion on the assigned cross-transitions. Rotational analysis of three bands of $Se^{80}O$ with $v'=2$ was done and the constants were obtained. The analysis suggests that the observed perturbation may be of homogeneous type. The details of high resolution work are presented in Chapter I(B).

The spectrum of SeN was not known by the time the work started. A direct combination of selenium and nitrogen in the sealed tube and excitation yielded a group of bands in the region $3960\overset{o}{A}$-$5675\overset{o}{A}$. At about the same time, Guy Pannetier and others (1965. C.R.Acad.Sci. (France), 260, 2155) reported some of the above bands attributable to NSe radical in a discharge of selenium tetrachloride and active nitrogen. Detailed investigations of low resolution and high resolution spectra of the observed bands, with enriched samples of selenium, proved that selenium is not involved in the emitter. However, no definite conclusions could be drawn on the nature of the emitter. Chapter II is devoted to the work on the above facts.

No high resolution work was known on Te_2 molecule. It is difficult to do any meaningful analysis because of the existence of several isotopes of Te. Recent investigations by Jha(1968) in this laboratory, revised the existing vibrational analysis of the near ultra-violet bands with the use of enriched isotopes of Te. Rotational analysis of some of the bands with v"=0 was done by him for Te_2^{130} in emission for the first time. The work on Te_2^{128} was taken up by the author and rotational analysis was done to confirm some of the observations of Jha on Te_2^{130} and in particular to look into finer details of the bands where perturbation occurs. A check of the rotational constants of Te_2^{130} could be made with the help of the obtained rotational constants for Te_2^{128}, though it was not possible to comment on the nature of the perturbation. Chapter III deals with the details of the high resolution work of Te_2^{128} molecule.

During the course of investigations some work was done on the $A^2_{\Pi} - X^2_{\Sigma}$ system of CaF molecule. Experiments with high current arc discharges have shown extra bands in the already known sequences of the system. Some comments are offered on the $\triangle$ v=+1 sequence. The details of the investigation are given in the last Chapter.

(K.V. Subbaram)

CONTENTS

CHAPTER I

CHAPTER I

ABSTRACT

The combination of selenium and oxygen in a sealed quartz discharge tube and excitation by a microwave oscillator yielded the spectrum of SeO molecule known in the near ultra-violet region. It was found that the second sub-band in the $v' = 2$ progression of the main system $A^3\Sigma^- - X^3\Sigma^-$ (Hund's case(b), large λ) was perturbed by about 28cm^{-1} and it was confirmed by the use of enriched isotopes of selenium. Certain new bands observed in the same region were assigined to cross-transitions of the above system. Rotatiònal analysis for the F_1-F_1 sub-band was performed for three bands (2-2), (2-3) and (2-4) and of the second sub-band for two bands (2-3) and (2-4). The corresponding rotational constants were obtained. It is suggested that the perturbation of the second sub-band may be of homogeneous nature.

A. PERTURBATION OF v=2 IN A $^3\Sigma^-$ OF SeO

INTRODUCTION

The emission spectrum of SeO has been studied in detail by Choong Shin Piaw (1938), Barrow and Deutsch (1963) and Haranath (1965). Barrow and Deutsch (1963) performed the rotational analysis and a correct vibrational numbering was assigned on the basis of the observed isotopic shift with separated isotopes of selenium. Their analysis shows the transition as $A\ ^3\Sigma^- - X\ ^3\Sigma^-$ (case b, large λ) so that the system splits up into two sub-systems $F_1 - F_1$ and $F_{2,3} - F_{2,3}$ (F_2 and F_3 components are lying very close, hence this notation) while no cross-transitions were reported. It was also concluded by them that SeO gets predissociated somewhere at $2 < v < 3$ in the excited state. The analysis of $F_1 - F_1$ sub-band for $v' = 2$ was done while no information was reported about $F_{2,3} - F_{2,3}$ sub-band.

In a general programme of work on certain Group VI compounds (SeO, SeN and Te_2) the emission spectrum of SeO under critical conditions showed clearly both the sub-bands $F_1 - F_1$ and $F_{2,3} - F_{2,3}$ of $v' = 2$ in $A\ ^3\Sigma^- - X\ ^3\Sigma^-$ system. However, the $F_{2,3} - F_{2,3}$ sub-band head was found displaced from its expected position indicating a large perturbation. With the availability of separated isotopes of selenium, it was felt that a complete analysis of bands with $v' = 2$ might give further information about the perturbation. The details of the investigation of vibrational analysis are discussed in this section and the details of high resolution work on $v' = 2$ level are given in section B. A discussion is also made on the assigned cross-transitions in this section.

EXPERIMENTAL

A direct combination of a few milligrams of the separated
isotopes of selenium obtained from the Oak Ridge National Labora-
tories, U.S.A. and about 5 to 6mm oxygen, in a sealed quartz tube
was found best suitable to excite the new bands. The sealed
quartz tube was prepared in a similar manner to that given by
Tomkins and Fred (1957) and Rao and Brody (1961). The procedure
of sealing is described below. This technique is employed through-
out the investigations except for the work in the last Chapter.

The discharge tube DT (Fig. I.1) was made of quartz tube
of about 9mm outer diameter and sealed out at one end. There was
a constriction in the discharge tube close to the other end. The
sample tube E was a pyrex tube of about 3.5mm outer diameter and
closed at one end. To the closed end of this tube, a small pyrex
tube containing an iron slug was attached. In the sample tube, a
few milligrams of selenium sample was put and the open end was
drawn into a capillary. The sample tube was then placed into the
side tube of a vacuum system which had a quartz to pyrex graded
seal GS. The open end of the quartz discharge tube was then fused
to the open end of the side tube of the vacuum system. The whole
system was evacuated with an oil diffusion pump. When a pressure
of the order of 10^{-5} mm was obtained with the sample tube in posi-
tion P_1, the discharge tube was degassed for several hours by
heating it to about $800^{\circ}C$ with the help of a laboratory built

furnace using a liquid nitrogen trap. After the degassing was over. the furnance was removed and the sample tube was moved with the help of a magnet to position P_2 so that its capillary projects into the discharge tube. The sample tube was then heated and a few milligrams of selenium sample was transferred into the discharge tube whose closed end is kept cool so that the hot selenium vapours settle at that end. The sample tube was then returned to position P_1. Then slowly about 5 to 6mm of oxygen gas was introduced into the discharge tube with the liquid nitrogen traps operating at the appropriate positions. The pressure of the gas entering the discharge tube was monitored with the help of a manometer connected to vacuum system. The discharge tube was then sealed off at the constriction. Sealed tubes of $Se^{80}O$ and $Se^{78}O$ were thus prepared.

The advantage of exciting the observed spectrum by the above discussed sealing technique is due to the following points: i) very small samples of the enriched substance could be effectively used without any wastage of the costly material, ii) the impurities which generally occur in conventional discharge tubes are eliminated to a considerable extent because of the elaborate and careful sealing procedure.

The discharge tube was excited by a Raytheon Microtherm microwave oscillator operating at 2450 Mc/s whose maximum power output is 100 watts. A 10 cm length of quartz tube of 11 cm outer

diameter served as the outer cover for the discharge tube for supporting it to rest on the central peg of the microwave antenna as shown in Fig. I.2. At first, with about 10% of the power, oxygen gas in the sealed tube was excited with the help of tesla discharge. This was the reason no other carrier gas such as Argon was used as a preexciting material. Now, by slowly increasing the power to about 50%, selenium started vapourizing and showing its own spectrum. At this stage, the power was slowly reduced to about 40% where one could see SeO bands extending into the visible region beyond 3900Å, with the help of a hand spectroscope.

As the second sub-band heads are comparatively weak the positions of the heads could be recognised only when photographed on low dispersion. The photograph showing these bands taken on a Zeiss medium quartz spectrograph at a dispersion of about 13Å/mm is shown in Fig. I.3. The figure shows the spectra taken with separated isotopes of selenium and the isotopic shift for all the recorded bands. Copper and iron arcs were used for wavelength calibrations. The measurements were done on a Zeiss Abbe comparator. The vacuum wavenumber data for all the band heads were obtained on an IBM-1620 computer using the standard formula incorporating Edlen's vacuum correction.

RESULTS AND DISCUSSION

We shall restrict our discussion to the bands with $v' = 2$ because these are the bands of present interest and a comparison is made wherever necessary to the bands in $v' = 0$ and $v' = 1$ progressions.

_even new bands involving $v' = 2$ are observed in the present experiments all of which show both $F_1 - F_1$ and $F_{2,3} - F_{2,3}$ sub-bands. The difference between these sub-bands is consistently of the order of 45 cm^{-1}, while in bands involving $v' = 0$ and $v' = 1$ the separation is of the order of $75 cm^{-1}$ and $70 cm^{-1}$ respectively. These values arise from the difference between the separations of the components F_1 and $F_{2,3}$ in $X^3 \Sigma^-$ and F_1 and $F_{2,3}$ in $A^3 \Sigma^-$. In other words, these are equal to a quantity $(2\lambda' - 2\lambda'')$ where $2\lambda'$ is the separation between the F_1 and $F_{2,3}$ levels in the excited state and $2\lambda''$ is the separation between the F_1 and $F_{2,3}$ levels in the ground state. λ indicates the strength of interaction between the total spin angular momentum S with the figure axis in triplet and other higher multiplet Σ states in Hund's case (b) approximation. Also the spin-spin interaction becomes quite appreciable and becomes an additional important contribution to the splitting of the levels. In this approximation, the F_2 and F_3 levels lie quite close and well separated from F_1 levels which separation is given by 2λ as discussed above. The energy expressions for F_1, F_2 and F_3 levels are given section B of this Chapter where the rotational analysis part is discussed.

Choong Shin Piaw (1938) was the first worker to observe the bands at $3084\overset{\circ}{A}$ and $3089\overset{\circ}{A}$ which happens to be the (2-3) band according to the revised numbering by Barlow and Deutsch (1963). The difference between these two sub-bands as reported by him is 43cm^{-1} which is of the same order as observed in the present investigations. Haranath (1965) maintained that all the bands with $v' = 2$ had 75cm^{-1} as the sub-band difference, similar to that in the $v' = 0$ and $v' = 1$ progressions. Using Se^{80} and Se^{78} separated isotopes in the present work, the sub-band difference of 45cm^{-1} in $v' = 2$ bands is confirmed for four bands (2-2), (2-3), (2-4) and (2-5) from the observation of expected isotopic shifts, which are shown in Fig. I.3. The isotopic shifts for both the sub-bands of $v' = 2$ are presented in Table I.1. The other observed bands in $Se^{80}O$ are (2-6), (2-9), (2-10) and (2-11)[*] with the same sub-band separation of about 45cm^{-1}. The isotopic shift data for these bands is not given because they were not well developed in the $Se^{78}O$ tube.

The separation of about 45cm^{-1} between the F_1-F_1 and $F_{2,3}$-$F_{2,3}$ heads of $v' = 2$ can be understood on the basis that the $F_{2,3}$ levels are shifted upwards as a whole by about 28cm^{-1} while the F_1 level was found to be undisplaced. This type of large displacements of the entire band are attributed to perturbations.

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[*]For $v' = 2$ this is the only common band between the data of Haranath (1965) and the present work. The separation of 45cm^{-1} was found clearly as is the case with other bands with $v'=2$.

In the present case, $\Delta G'_{3/2}$ of the $F_{2,3}$ component was found to be about 533.3cm^{-1} while the corresponding $\Delta G'_{1/2}$ was about 515.5cm^{-1} thus indicating an increase of about 18cm^{-1}. One such case of increase in vibrational frequency was in γ-system of NS molecule found by Narasimham and Srikameswaran (1962).

As reported by the earlier workers, no bands were observed for $v' > 2$ thereby indicating that the molecule is probably predissociated for $2 < v' < 3$.

Other well developed bands observed in this investigation are (0-3), (0-4), (1-2) which are shown in Fig. I.3 and (1-10) band (not shown in the figure). All the observed bands of $Se^{80}O$ are given in a Deslandre's Table (Table I.2) which also includes the already known bands. The measurements are from a plate taken on a 1m. Jaco grating spectrograph at a dispersion of about $18\text{Å}/\text{mm}$.

Assigned Cross-Transitions:

There are six additional bands in the same region with similar structure. It was not possible to incorporate them in the same vibrational scheme for $A^3\Sigma^- - X^3\Sigma^-$ and one can state that these do not come either from F_1-F_1 or $F_{2,3}-F_{2,3}$ transitions of the main system. Their presence due to some impurity is also ruled out from the observed isotope shifts when the experiments were conducted with separated isotopes of selenium, indicating thereby that they belong to a compound where selenium is one of

the constituents. The wave number data of these bands from both isotopes is given in Table I.3. Instead of assuming that these bands might arise from a new electronic state at about the same place as that of v=2 of $A^3 \Sigma^-_u$, an attempt was made to fit whether they could arise from cross-transitions such as $0^+(F_1) - 1(F_{2,3})$ and $1(F_{2,3}) - 0^+(F_1)$ belonging to the same main system $A^3\Sigma^-_u - X^3\Sigma^-_g$, both the states tending to acquire the properties of Hund's coupling case (c).

The $A^3\Sigma^-$ and $X^3\Sigma^-$ states (case b, large λ) could be approximated to case (c) coupling, if not to a pure case (c) coupling. While O_2 and S_2 molecules strictly belong to case (b), in Se_2 the states go over to case (c) whose λ value is estimated to be very large by Barrow and others (1966). They also have reported that the $1_u - 1_g$ sub-system is rather weak compared to the $0^+_u - 0^+_g$ sub-system which could be correlated to the fact that the 1_u component is less populated. No cross transitions have been reported by them though the selection rules permit them. In the present analysis three of the six bands mentioned above could be explained as arising due to transitions from 1 component of v=2 in $A^3\Sigma^-_u$ to 0^+ component of $X^3\Sigma^-$. The designations of these bands are (2-2), (2-3) and (2-4) and they are shown in Fig. I.3. This assignment is further explained as follows: The λ_v values in the ground state are known according to Barrow and Deutsch (1963). A cross-transition of the type $F_{2,3}(1) - F_1''(0^+)$ can be obtained from the following relation given by $F_{2,3}'(1) - F_1''(0^+) = F_{2,3}'(1) - F_{2,3}''(1)$

plus the corresponding 2 λ_v value in the ground state. In the present case, the second sub-bands of (2-2), (2-3) and (2-4) of the main system are chosen and the corresponding 2 λ_v'' values are used to explain the observed bands. It is of interest to note that $F_{2,3}$ level in v=2 of $A^3\Sigma^-$ is the state that is perturbed which happens to be the initial level of the above assigned transitions. The reasonably accurate fit of these bands confirms further the positions of all levels in $F_{2,3}$-$F_{2,3}$ sub-band of v'=2 bands. At this stage, the following comments may be made: i) F_1, $F_{2,3}$ levels in the upper state, being not far away could reach an equilibrium among themselves thereby increasing the chance of observation for the cross-transitions ii) The perturbed state being a mixed state itself probably enhanced the transition probability for otherwise weak transitions. The band at 31744cm^{-1} can be interpreted as v=1, 0^+ (A $^3\Sigma^-$) $\rightarrow$ v=3,1 ($X^3\Sigma^-$). There is some uncertainity with respect to the bands at 32613 cm^{-1} and 33507cm^{-1}. Probably they belong to v=1, 0^+ ($A^3\Sigma^-$) $\rightarrow$ v=2, 1 ($X^3\Sigma^-$) and v=1, 0^+ ($A^3\Sigma^-$) $\rightarrow$ v=1, 1 ($X^3\Sigma^-$), though the head measurements do not agree well with the expected values. Cross-transitions from other progressions and involving other sub-band heads, however, have not been observed.

B. ROTATIONAL ANALYSIS OF CERTAIN BANDS
WITH $v'=2$ IN $A^3\Sigma^- - X\,^3\Sigma^-$ SYSTEM OF $Se^{80}O$

INTRODUCTION

Barrow and Deutsch (1963) performed the rotational analysis of two bands (2-9) and (2-10) of SeO in addition to the bands involving $v'=0$ and $v'=1$ progressions and gave the rotational constant of the level $v'=2$ for the F_1-F_1 sub-band. However, no analysis on the second sub-band $F_{2,3}-F_{2,3}$ with $v'=2$ was given by them.

As was discussed in section A of this Chapter, the emission spectrum of SeO under critical conditions showed clearly both the sub-bands F_1-F_1 and $F_{2,3}-F_{2,3}$ of $v'=2$ in $A^3\Sigma^- - X^3\Sigma^-$ system with a large perturbation for second sub-band. It was felt that the analysis of the second sub-band might reveal the nature of perturbation. Attempts were made to photograph the high resolution spectra of three bands (2-2), (2-3) and (2-4) which were well developed and there was not much overlapping from neighbouring bands. The rotational analysis of the F_1-F_1 sub-band of $Se^{80}O$ was done and the constants were obtained. It was possible to do partly the rotational analysis of the $F_{2,3}-F_{2,3}$ sub-band in (2-3) and (2-4) bands and rotational constants were obtained.

The details of the procedure of rotational analysis, evaluation of rotational constants and a discussion on the perturbations are given in this section.

EXPERIMENTAL

The spectrum of $Se^{80}O$ was excited in a sealed quartz tube, the details of which are given in section A of this Chapter, by the microwave oscillator operating at 2450 Mc/s and a power of about 40 watts was sufficient to get the best condition for the excitation of the bands. The high resolution spectrum of (2-2), (2-3) and (2-4) bands in the 3000$\overset{o}{A}$ - 3200$\overset{o}{A}$ region was recorded in the III order of a 3.4 meter Jaco grating spectrograph using a 4" grating (30,000lpi) blazed for 10,000$\overset{o}{A}$ at a dispersion of about 0.6$\overset{o}{A}$/mm. The exposure timings for best spectra varied from one to three hours on Kodak 103a-O plates and the exposures were given so as to have least overlapping from the first head because the second head is comparatively weaker. Iron arc from a D.C. source was used for wavelength calibrations. The measurements were done on a Zeiss Abbe comparator. All the calculations of vacuum wavenumbers of the rotational lines were done on an IBM computer. The accuracy of the measurements was found to be $\pm$ 0.02 cm^{-1} for the sharp rotational lines and $\pm$ 0.04cm^{-1} for the lines which are broad.

ROTATIONAL ANALYSIS

The details of the following discussion on rotational structure are given with the help of Herzberg (1950).

<u>General Relations</u>:   The total energy E of a molecule can be written as a sum of Electronic energy, vibrational energy and rotational energy,taking into account the appropriate inter-action between electronic motions and vibrational and rotat-ional motions of the nuclei. The following relation for the frequencies in electronic spectra

$$\mathcal{V} = \mathcal{V}_e + \mathcal{V}_v + \mathcal{V}_r \qquad \text{I.1}$$

would then give a quantity $\mathcal{V}_0 = \mathcal{V}_e + \mathcal{V}_v$ called "band origin" and is a constant for the particular vibrational tran-sition between the electronic states under consideration. If one observes a transition from an upper state to a lower state, the frequency of the line is given by

$$\mathcal{V} = \mathcal{V}_0 + F'(J') - F''(J'') \qquad \text{I.2}$$

where $F'(J')$ and $F''(J'')$ are the rotational term values in the upper and lower electronic states. In general, the rotational levels of a $^3\Sigma$ state in Hund's case (b) approximation are re-presented by the following relations (Herzberg, 1950) ignoring the contribution from the centrifugal distortion constant (D).

$$F_1(K) = B_v K(K+1)+(2K+3)B_v - \lambda - \sqrt{(2K+3)^2 B_v^2 + \lambda^2 - 2\lambda B_v} \qquad)$$
$$+\gamma(K+1) \qquad\qquad)$$
$$)$$
$$)$$
$$)$$
$$F_2(K) = B_v K(K+1) \qquad\qquad)$$
$$)$$
$$)$$
$$F_3(K) = B_v K(K+1)-(2K-1)B_v - \lambda + \sqrt{(2K+3)^2 B_v^2 + \lambda^2 - 2\lambda B_v - \gamma K})$$

I.3

where F_1, F_2 and F_3 refer to the levels with J=K+1, K and K-1 respectively. K is component of Λ on the internuclear axis. Since the total electron spin is 1, each level with K splits into three levels with J=K+1, K and K-1. λ and γ are known as splitting constants and B_v is the rotational constant. The contribution of λ is due to spin-spin interaction. It is known that the main system of SeO molecule belongs to Hund's case (b) type of coupling with a large λ value, compared to the B value. In this approximation, eqns (I.2) can be rewritten as

$$F_1(K) = B_v K(K+1) + (2K+3) B_v - 2\lambda$$
$$F_2(K) = B_v K(K+1)$$
$$F_3(K) = B_v K(K+1) - (2K-1) B_v$$

I.4

neglecting γ which is very small.

The above expressions can be again written in the J co-ordinates, after taking the influence of spin into consideration, as follows:

$$F_1 = B_v J(J+1) - 2\lambda$$
$$F_{2,3} = B_v J(J+1)$$

I.5

for a particular K value.

From eqns (I.5) it is clear that when λ is very large compared to B_v, the rotational constant, F_1 levels get separated

from F_2 and F_3 levels for a particular K value and the separation is equivalent to a quantity $2'\lambda$. However, this quantity could have different magnitude in the excited state and the ground state.

The branches of a band are obtained by using following selection rules in Hund's case (b) approximation.

$$\triangle K = \pm 1$$

where branches for which $\triangle K = \triangle J$ are most intense. The branches for which $\triangle K = +1$ and $\triangle J = +1$ are known as R branches and $\triangle K = -1$ and $\triangle J = -1$ are known as P branches. From eqn I.5, apart from the constant factor 2λ, the following expressions could be written for R and P branches using eqn (I.2)

$$
\begin{aligned}
R(J) &= \nu_0 + 2B_v' + (3B_v'-B_v'') J + (B_v'-B_v'') J^2 \quad) \\
& \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad) \quad I.6 \\
P(J) &= \nu_0 \qquad\quad - (B_v'+B_v'') J + (B_v'-B_v'') J^2 \quad)
\end{aligned}
$$

The P and R branches could be represented by a single formula

$$\nu = \nu_0 + (B_v'+B_v'') m + (B_v'-B_v'') m^2 \qquad I.7$$

where $m = -J$ for the P branch and $m = J+1$ for the R branch.

Thus in SeO, from the above discussion one expects six main branches R_1, R_2 and R_3 and P_1, P_2 and P_3 where R_2 and R_3 lie quite close as do P_2 and P_3 and well separated from R_1 and P_1 respectively. The band with R_1 and P_1 branches is designated F_1-F_1 sub-band and with R_2, R_3 and P_2, P_3 branches as $F_{2,3}-F_{2,3}$ sub-band.

$F_1 - F_1$ sub-band:

In all the three bands (2-2), (2-3) and (2-4) for which the high resolution spectrum is photographed, this sub-band consisted of single P and R branches as is also the case in the bands in $v' = 0$ and $v' = 1$ progressions.

After the P and R branches are picked up, combination relations were formed to obtain separately the upper and lower state rotational levels from the observed lines and then to evaluate rotational constants.

Since all the observed bands have a common upper level, the following combination relation was employed

$$\triangle_2 F' = R(J) - P(J) = (4B_v' - 6D_v')(J + \tfrac{1}{2}) - 8D_v'(J + \tfrac{1}{2})^3 \qquad I.8$$

taking the contribution of D_v, the centrifugal distortion constant which is often much smaller than B_v, the rotational constant.

Since many sets of combination relations can be formed with the help of the observed series, the method of least squares was employed to find the correct set with the help of eqn.(I.8) neglecting the contribution of D_v. Once the correct set of combination differences is decided it was proceeded to fix the J numbering for the levels, because we have been operating till now with an arbitrary numbering.

From relation (I.8) one can see that if one draws a graph

of $\triangle_2 F'$ (neglecting D_v) vs. an arbitary running number, it is

clear that the straight line should cut the abscissa axis at $J=-\frac{1}{2}$

and the adjustment of this axis is done till it does so. This

method of fixing the J numbering is fairly accurate and the error

could be ± 1 in the numbering.

However, there is a sensitive test to fix the absolute J

numbering. Using again eqn.(I.8), the plot of $\triangle_2 F'/J+\frac{1}{2}$ vs $(J+\frac{1}{2})^2$

should give a straight line, the intercept giving the value of

$(4B_v'-6D_v')$ and the slope the value of $8D_v'$. If there is no contri-

bution due to D_v, this line will be parallel to the abscissa axis.

This straight line will assume the form a curve at low J values,

if the numbering is off even by 1. (If J is off by +1, convex

shape results and -1 gives a concave shape). From the above graph,

apart from fixing the absolute J numbering one can also find the

molecular constants B_v and D_v.

The wavenumbers for the three bands with J numbering

are presented in Table I.4. The set of combination differences

obtained by the least squares method is given in Table I.5. The

rotational structure of one band (2-4) is shown in Fig. I.4 and the

R and P branches for F_1-F_1 sub-band are marked. The graph for

fixing the correct J numbering and finding the rotational constants

for $v'=2$ level of this sub-band is shown in Fig. I.5. The B value

diff s by 0 004 m ^{1} from the val e obt d by B o v ɔ d Deutsch
(1963) vhicl they g t from tl f st s b b d of (2 9) nl (2 10)
ba ds

D t m t o of Ba d Or g ns

Whel 11 th J lucs a e present in a ba d d ʋ th
nlʃ a P ɔnd Γ branch the following relation is formed

$$R(J\ 1) + P(J) = 2\ )_{0} + 2(B_{v} - B_{v}\ )\ J^{2} \qquad I\ 9$$

Vhen $R(J-1) + P(J)$ s plotted ɔg nst J^{2} a st a ght l ne is obt i ed
whose intercept with the o dinate axis gives 2 $)_{0}$ and the slope gives
tl e quantity $2(B_{v}\ B_{v}\ )$ Such g pls for (2 2) (2-3) and (2-4) bands
ɔre shown i Fig I 6 (a) (b) and (c) respectively The v lues
from Band origin graphs ar tabul ted in Table I 7 By k owing the
value of B for v =2 ɔ d the val s of $(B_{v}\ B_{v}\ )$ for (2 2) (2 3)
a d (2 4) b nds tl e rotat al const rts foɩ the levels ʋ = 2 3
ɔnd 4 we c d termined for the fi st time All the c stants obtained
in tl s l sis are sɩm ar zed n Table I 8 A comparison is made
ʋ l ereve nec ss y ʋ ith the values obtaɩ ed by calc lating the
constants f om tl e fo mula given by Barrow and Deutsch (1963) ɔ d
tl e ɔgree ent wɐs found to be good

Sɩcond Sɩb bɔ d

It wɔs not easy to pick up the braɩches in this sub band
because t is pertu bed heavily in terms of displaceme t and ı tens
ıty The identıf ed P and R branches in two baɩds (2 3) and (2 4)

are given in Table I.6 along with the J numbering. The R and P branches are shown in Fig. I.4 for the (2-4) band. The combination diffe⁻ences were formed and best set was chosen following the procedure as discussed in case of F_1-F_1 sub-band and this set is shown in Table I.5. The rotational constants are obtained after fixing the correct J numbering by drawing a graph of $\triangle_2 F'/J+\frac{1}{2}$ vs $(J+\frac{1}{2})^2$ and is shown in Fig. I.7. The band origin graphs for the sub-bands are drawn in Fig. I.8 (a) and (b).

The rotational constants are summarized in Table I.8 and compared with those obtained by calculating from the formulae given by Barrow and Deutsch (1963) for the v"=3 and v"=4 in F_2-F_2 sub-band. Such a comparison of B values has shown that the branches picked up belong to F_2- F_2 sub-band. It was not possible to pick up any lines of F_3-F_3 sub-band.

A check for all the constants obtained by graphical method could be made on an IBM-7044 computer incorporating a least square fit programme and good agreement was found for the band origins and the rotational constants.

Perturbations:

Perturbations are known as abnormalities in otherwise smooth course of the branches in one or several successive lines of a branch. Sometimes even a splitting into two lines appears, or for multiplet bands the multiplet splitting may be abnormally large or small at a

certain place or certain places in the band. Apart from the deviation from the normal course, an intensity change may also be associated sometimes or the intensity change may appear alone independently. A resonance like behaviour is noticed when perturbations occur for a number of successive J values. Thus we have intensity changes as well as displacements for the rotational lines when perturbations occur in a band system. The perturbations in the band fine structure are due to perturbations in the rotational term series either of the upper or of the lower state. So, if a perturbation appears at a certain point in a P branch of a band, it will also reflect in the corresponding R branch of the band and will have the same type and magnitude.

Mulliken (1937) has categorised the perturbations into two types. Perturbations with $\triangle \wedge = 0$ are perturbations between states of the same type and are called homogeneous perturbations and those between unlike states i.e., $\triangle \wedge = \pm 1$ are called heterogeneous perturbations. While heterogeneous perturbations can arise only on account of the finer interaction of rotation and electronic motion, the homogeneous perturbations occur even when this interaction is neglected. Experimentally it is possible to distinguish between the two cases from a closer study of perturbations and one can arrive at definite conclusions about the nature of the perturbing state even if transitions are not observed from this state directly.

$F_1 - F_1$ Sub-band:

Barrow and Deutsch (1963) have observed that in SeO,
the perturbation in $v'=2$ level of $F_1 - F_1$ sub-band is at $J = 25$
but however, they were not sure about it. In this analysis, it
was found that the level at $J = 27$ in $v' = 2$ has been found to
be displaced apart from another displacement at $J = 37$ in the
same vibrational level. The $\underset{\wedge}{/}$ lines are marked separately in
Corresponding
Fig. I.4. From the analysis of the bands with $v'=0$ in $F_1 - F_1$
sub-band and observing perturbations at closeby J values, they
have suggested that the perturbing state might be a multiplet
state $^3\eta_l$ (Hund's case (b)). No direct evidence for this fact
has been observed from the present analysis, but it is quite
likely that the same perturbation is responsible for the $v'=1$
and $v'=2$ progressions also in the $F_1 - F_1$ sub-band of the main
system of SeO molecule.

$F_2 - F_2$ Sub-band:

It can be seen from Table I.7 that there is random
variation in the first differences of $\triangle_2 F'(J)$ values. This
indicates that there is small but definite displacement among
the rotational levels themselves apart from the fact that the
band is shifted as a whole by about 28cm^{-1}. Such large displa-
cements in the bands are attributed generally to homogeneous
perturbations. In such a case, the avoidance of crossing of

potential energy curves of similar species (i.e. $\Delta \Lambda= 0$ and

$\Delta \Sigma = 0$) for the perturbed and perturbing states results in a

situation that the final states having combined properties of

both. It is not very clear that it is a homogeneous perturbat-

ion by comparing the B values to those for v=0 and v=1 in the

upper state in $F_2 - F_2$ sub-band obtained by Barrow and Deutsch

(1963). It is found larger than what would be expected from the
though
calculated value/consistent with the fact that with an increase

in vibrational frequency the rotational constant also increases.

The value of rotational constant for v'=2 is expected to be $0.26cm^{-1}$

whereas the value obtained from the present analysis is $0.295cm^{-1}$.

If it is a homogeneous perturbation, it could be only from another

$^1\pi$ state because the $F_{2,3} - F_{2,3}$ sub-band assumes the properties

of a $^1\pi$ state, in Hund's case (b), large λ . However, the

situation is not entirely clear since one can have many states

perturbing the $A^3 \Sigma^-$ state of SeO.

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Table I.1   - Isotopic shifts (in cm^{-1}) for $v' = 2$ bands of $A\ ^3\Sigma^-_u - X\ ^3\Sigma^-_g$ system of SeO molecule

$v'-v''$	F_1-F_1				$F_{2,3}-F_{2,3}$			
	$Se^{80}O$	$S_{Se}^{78}O$	$\Delta\nu'$ Obs.	$\Delta\nu'$ Cal.	$Se^{80}O$	$Se^{78}O$	$\Delta\nu'$ Obs.	$\Delta\nu'$ Cal.
2-2	33303.5	33301.3	2.2	2.1	33258.5	33256.2	2.3	2.1
2-3	32415.4	32411.4	4.0	3.9	32369.8	32365.4	4.4	3.9
2-4	31538.1	31532.2	5.9	5.6	31493.4	31487.6	5.8	5.6
2-5	30666.8	30659.0	7.8	7.5	30621.7	30613.5	8.2	7.5
2-6	29806.5	-	-	-	29764.1	-	-	-
2-9	27275.4	-	-	-	27232.2	-	-	-
2-10	26454.3	-	-	-	26410.0	-	-	-
2-11	25636.5	-	-	-	25594.3	-	-	-

T bl I 2   D l d   hem f h b

	2	3		5	6	7	8	9
0		31399 881	30518 872	29646 861	28785 852	27933 841	27092 833	2625?
		75	75	73	73	73	74	75
		31324 881	30443 870	28712 852	27860 842	27018 834	26184 825	2535?
ΔG_{γ}		511	512	515	514	512		
		515	517	517	516	514		—
1	32800 890	31910 880	31030 869	30161 862	29299 854	28445		—
	72	71	70	71	71	71		—
	32728 889	31839 879	30960 870	30090 862	29228 854	28374		—
$\Delta G'_{3/2}$	504	505	508	506	501		—	—
	531	531	533	532	532		—	—
2	33304 889	32415 877	31538 871	30667* 867	29800			27275
	45	45	45	45	40			42
	33259 889	32370 877	31493 871	30622 862	29760*		—	2723?

Th b d   k d ith t i k

h d f S $^{80}_{0}$ A^3→ X^3∑ y t

	ↄ	11	12	13	14	15
824 2543	815 24620	810 23810	798 23012	782 22230		
76	75	76	75	75		
825 25359	814 24545	811 23734	797 22937	782 22155		
510	510	514	514	510		
514	515	518	516	513		
25945	815 25130	806 24324	798 23526	786 22740	784 21956	
72	70	72	73	72	73	
25873	813 25060	808 24252	799 23453	785 22668	785 21883	
5??	508					
537	535					
821 26454	816 25638					
44	43					
822 26410	816 25595					

th   ly b   d h d
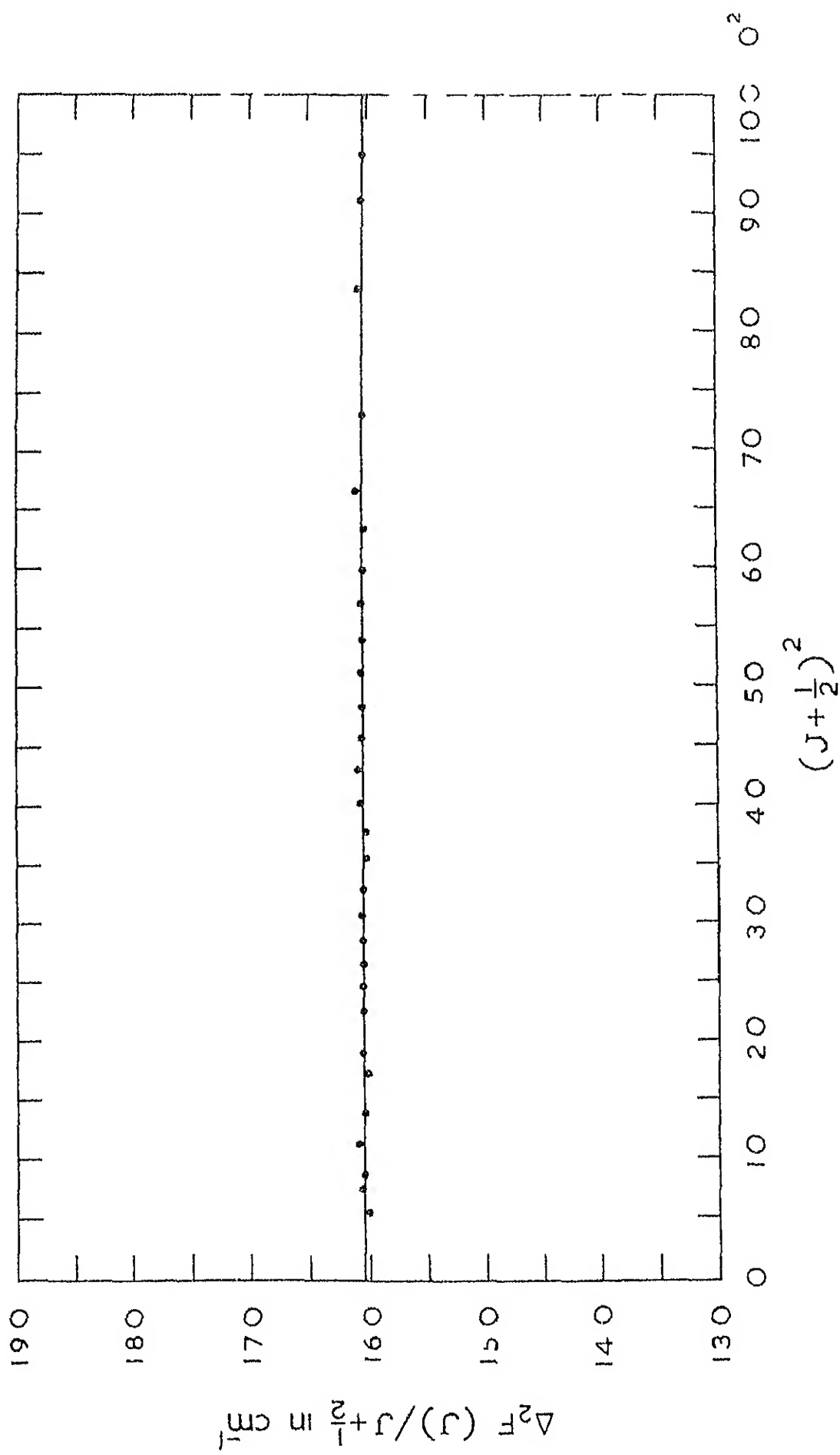
Fig III 3 — GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS AND
CHECKING OF J NUMBERING for $v=0$ of Te_2^{128}

$(J+\frac{1}{2})^2$

$\Delta_2 F\,(J)/J+\frac{1}{2}$ in cm^{-1}

61

Fig III 4 (d) GRAPHICAL DETERMINATION OF THE BAND ORICIN

Ig Ⅲ 4(f) GRAPHICAL DETERMINATION OF THE BAND ORIGIN

Table I.3—Assigned cross-transitions and isotopic shifts in cm⁻¹

	$0^+(A^3\Sigma^-) - 1(X^3\Sigma^-)$					$1(A^3\Sigma^-) - 0^+(X^3\Sigma^-)$			
v',v"	Se^{80}_0 exp.position	Se^{80}_0 obs.	Se^{78}_0 obs.	$\Delta\nu^i$	v',v"	Se^{80}_0 exp.position	Se^{80}_0 obs.	Se^{78}_0 obs.	$\Delta\nu^i$
1,1	33526.0	33510.2	33507.1	3.1	2,2	33432.0	33436.2	33433.2	3.0
1,2	32626.5	32617.0	32612.7	4.3	2,3	32544.2	32548.5	32544.0	4.5
1,3	31735.6	31746.7	31744.0	2.7	2,4	31660.4	31660.9	31658.8	2.1

Table I.4—Wavenumbers of rotational lines for F_1-F_1 sub-band of Se^{80}O.

J	2-2 R(J)	2-2 P(J)	2-3 R(J)	2-3 P(J)	2-4 R(J)	2-4 P(J)
4					31533.63	31528.32
5					32.70	26.27
6					31.43	23.77
7					29.72	20.97
8			32406;12	32396;27	27.84	17.96
9			03.85	92.77	25.45	14.31
10	33288.36	33276.22	01.14	88.96	22.92	10.76
11	85.39	72.03	32398.16	84.79	20.00	06.62
12	81.94	67.52	94.85	80.35	16.66	02.18
13	78.18	62.57	91.20	75.46	13.10	31497.47
14	74.13	57.40	87.15	70.37	09.18	92.46
15	69.58	51.65	82.77	64.83	04.94	86.97
16	64.90	45.81	78.07	59.00	00.29	81.28
17	59.67	39.31	73.08	52.82	31495.41	75.29
18	54.04	32.71	67.62	46.29	90.15	68.81
19	48.27	25.94	61.87	39.48	84.52	62.04
20	42.31	18.71	55.87	32.29	78.67	55.04
21	35.54	10.90	49.44	24.83	72.23	47.55
22	28.65	02.86	42.67	16.93	65.57	39.80
23	21.34	33194.41	35.54	08.59	58.66	31.65
24	13.76	85.81	28.06	00.04	51.35	23.35
25	05.52	76.64	19.99	32291.10	43.42	14.57
26	33197.45	56.11	12.17	81.76	35.70	05.43
27	88.79	57.17	03.61	71.94	27.40	31395.82
28	79.72	47.43	32294.66	62.34	18.77	86.42
29	70.24	36.72	85.37	51.85	09.57	76.10
30	60.49	25.81	75.84	41.18	00.24	65.63
31	50.10	14.46	65.72	30.08	31390.36	54.73
32	39.60	02.98	55.29	18.70	80.17	43.62
33	28.54	33090.89	44.59	06.82	69.62	31.91
34	17.10	78.40	33.28	32194.57	58.71	20.00
35	05.11	—	21.54	81.94	47.09	07.60
36	3309?.??	52.35	08.79	68.94	34.46	31294.87
37		38.62	32197.28	55.34	22.95	81.50
38		23.90	84.78	40.76	10.56	67.08
39			71.76		31297.58	
40			58.55		84.30	
41			45.00		70.73	

Table I.5-Combination differences $\Delta_2F'(J)$ for $v'=2$ of Se^{80}O

J	2-2	F_1-F_1 sub-band 2-3	2-4	Average	F_2-F_2 sub-band 2-3	2-4	Average
4			5.31	5.31		5.84	5.84
5			6.43	6.43		7.01	7.01
6			7.66	7.66		7.95	7.95
7			8.75	8.75	9.18	9.09	9.13
8		9.85	9.88	9.87	10.44	10.01	10.23
9		11.08	11.14	11.11	10.74	10.62	10.68
10	12.14	12.18	12.16	12.16	11.78	11.93	11.85
11	13.36	13.37	13.38	13.37	12.94	12.91	12.92
12	14.42	14.50	14.48	14.47	14.47	14.48	14.48
13	15.61	15.74	15.63	15.66	15.48	15.52	15.50
14	16.73	16.78	16.72	16.74	16.61	16.58	16.60
15	17.93	17.94	17.97	17.95	18.32	18.01	18.16
16	19.09	19.07	19.01	19.06	19.55	19.56	19.56
17	20.36	20.26	20.12	20.25	20.97	21.14	21.06
18	21.33	21.33	21.34	21.33	22.38	22.47	22.43
19	22.33	22.39	22.48	22.40	24.61	24.23	24.42
20	23.60	23.58	23.63	23.60	25.07	24.90	24.98
21	24.64	24.61	24.68	24.64	26.83	26.32	26.58
22	25.79	25.74	25.77	25.77	27.53	27.53	27.53
23	26.93	26.95	27.01	26.96	28.98	28.83	28.91
24	27.95	28.02	28.00	27.99	30.13	30.01	30.07
25	28.88	28.89	28.85	28.87		31.60	31.60
26	30.34	30.41	30.27	30.34		32.52	32.52
27	31.62	31.67	31.58	31.62			
28	32.29	32.32	32.35	32.32			
29	33.52	33.52	33.47	33.50			
30	34.68	34.66	34.61	34.65			
31	35.64	35.64	35.63	35.64			
32	36.62	36.59	36.55	36.59			
33	37.65	37.77	37.71	37.71			
34	38.70	38.71	38.71	38.71			
35	-	39.60	39.50	39.55			
36	39.76	39.85	39.60	39.73			
37		41.94	41.45	41.70			
38		44.02	43.48	43.75			

Table I.6 - Wavenumbers of Rotational Lines for $Se^{80}O$ in $F_2\text{-}F_2$ sub-band

J	2-3 R(J)	2-3 P(J)	2-4 R(J)	2-4 P(J)
4			31492.46	31486.62
5			91.53	84.52
6			90.15	82.20
7	32367.62	32358.44	88.53	79.44
8	65.58	55.14	86.62	76.52
9	63.58	52.84	84.52	72.90
10	61.22	49.44	82.20	70.27
11	58.44	45.50	79.44	66.53
12	55.14	40.67	76.52	62.04
13	51.02	35.54	72.90	57.38
14	47.22	30.61	68.81	52.23
15	43.15	24.83	64.47	46.46
16	38.35	18.80	59.85	40.29
17	33.14	12.17	55.04	33.90
18	27.69	05.31	49.87	27.40
19	21.62	32297.01	44.16	19.93
20	15.31	90.24	37.16	12.26
21	08.59	81.76	30.66	04.34
22	01.36	73.83	23.35	31395.82
23	32293.82	64.84	16.11	87.28
24	85.75	55.62	08.21	78.20
25			00.24	68.64
26			31391.13	58.61
27			82.06	
28			72.49	

Table I.7 - values from Band origin graphs (in cm^{-1})

$v' - v''$	$F_1 - F_1$		$F_2 - F_2$	
	ν_0	$-(B_v' - B_v'')$	ν_0	$-(B_v' - B_v'')$
2-2	33301.00	0.1658	-	-
2-3	32412.50	0.1620	32372.00	0.1645
2-4	31534.00	0.1584	31493.50	0.1611

Table I.8 - Rotational constants of $Se^{80}O$ (in cm^{-1})

	$F_1 - F_1$		$F_2 - F_2$	
	Present value	Calculated from Barrow's formula	Present value	Calculated from Barrow's formula
B_2''	0.4578	0.4575	-	-
B_3''	0.4540	0.4543	0.4595	0.4592
B_4''	0.4504	0.4511	0.4561	0.4560
B_2'	0.2920	0.2880 (obtained by Barrow)	0.2950	0.2601

Iron slug E Sample

E -   sample tube

Pyrex   Quartz   T   D

To
vacuum system

P₁   GS   P₂   Quartz Discharge
tube

Fig 1 1

Quartz tube
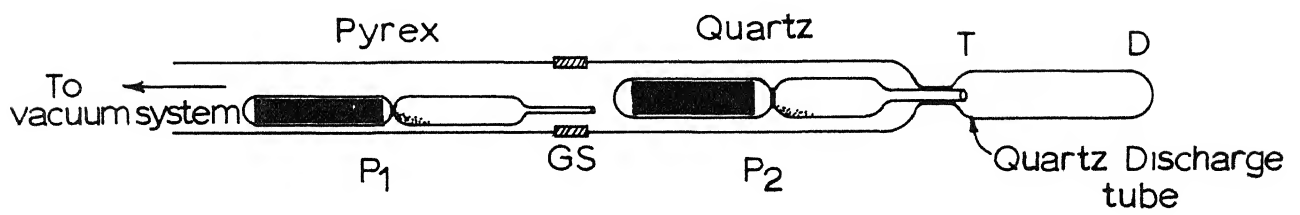
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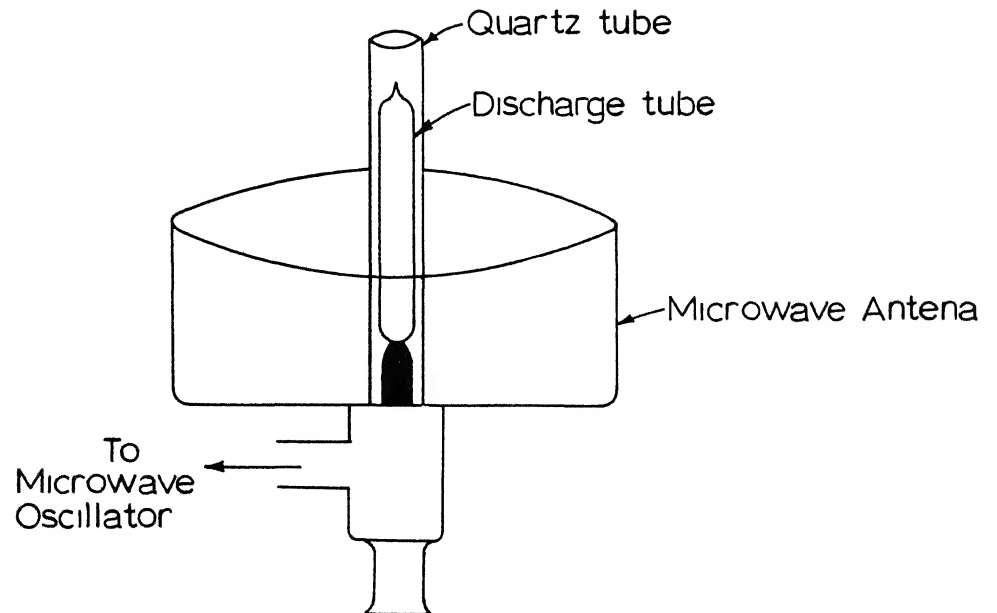
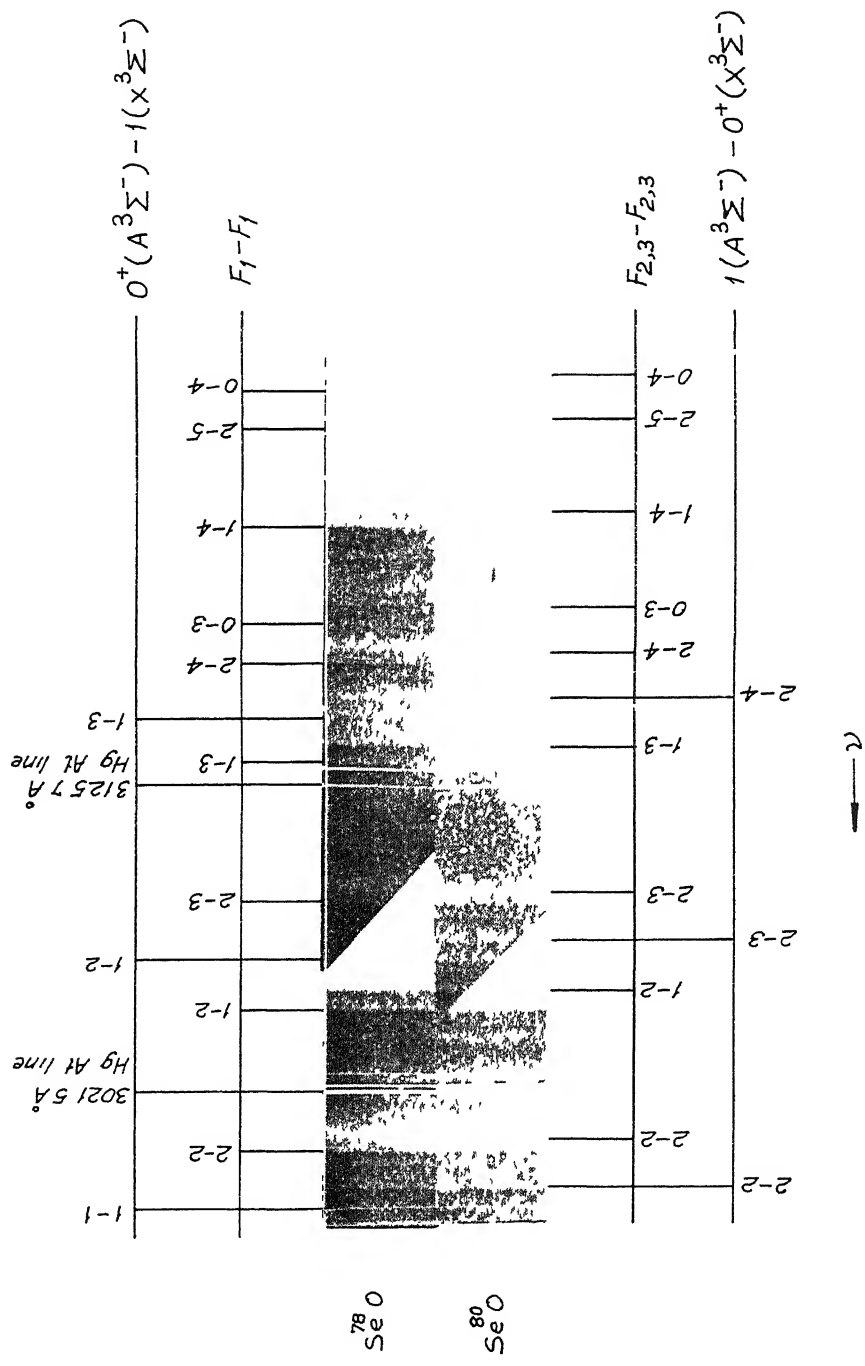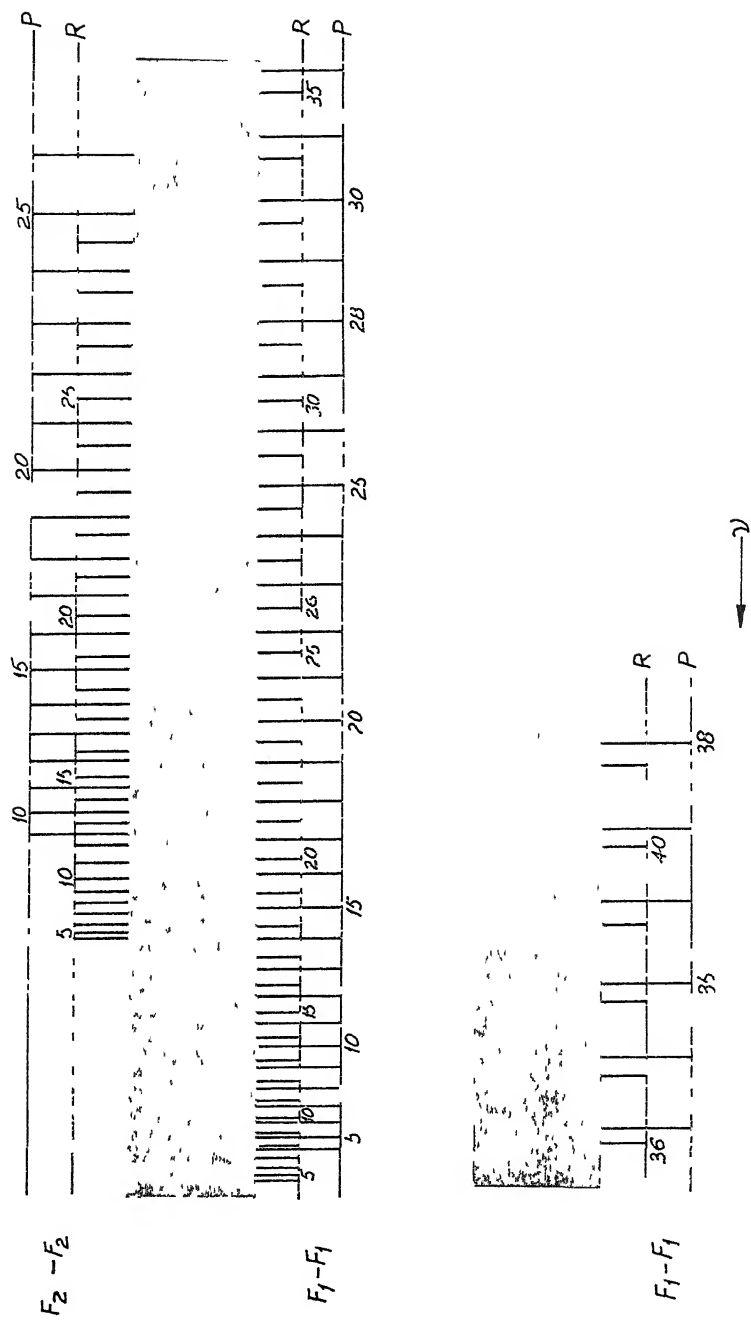Microwave Antena

To
Microwave
Oscillator
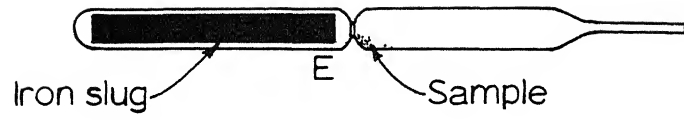
Fig 1 2

Fig I 3 Photograph of SeO on Medium Quartz spectrograph with separated isotopes of selenium showing the perturbation of $V=2$, $A^3\Sigma^-$ and the assigned cross-transitions

FigI 4 Rotational Structure of (2,4) band of SeO^{80} showing F_1-F_1 and F_2-F_2 sub-bands and perturbations at R(26),R(36), P(28) and P(38) in F_1-F_1 sub-band Photograph taken in the III order of a Jarrell-Ash grating spectrograph at a dispersion of 0 6 Å/mm
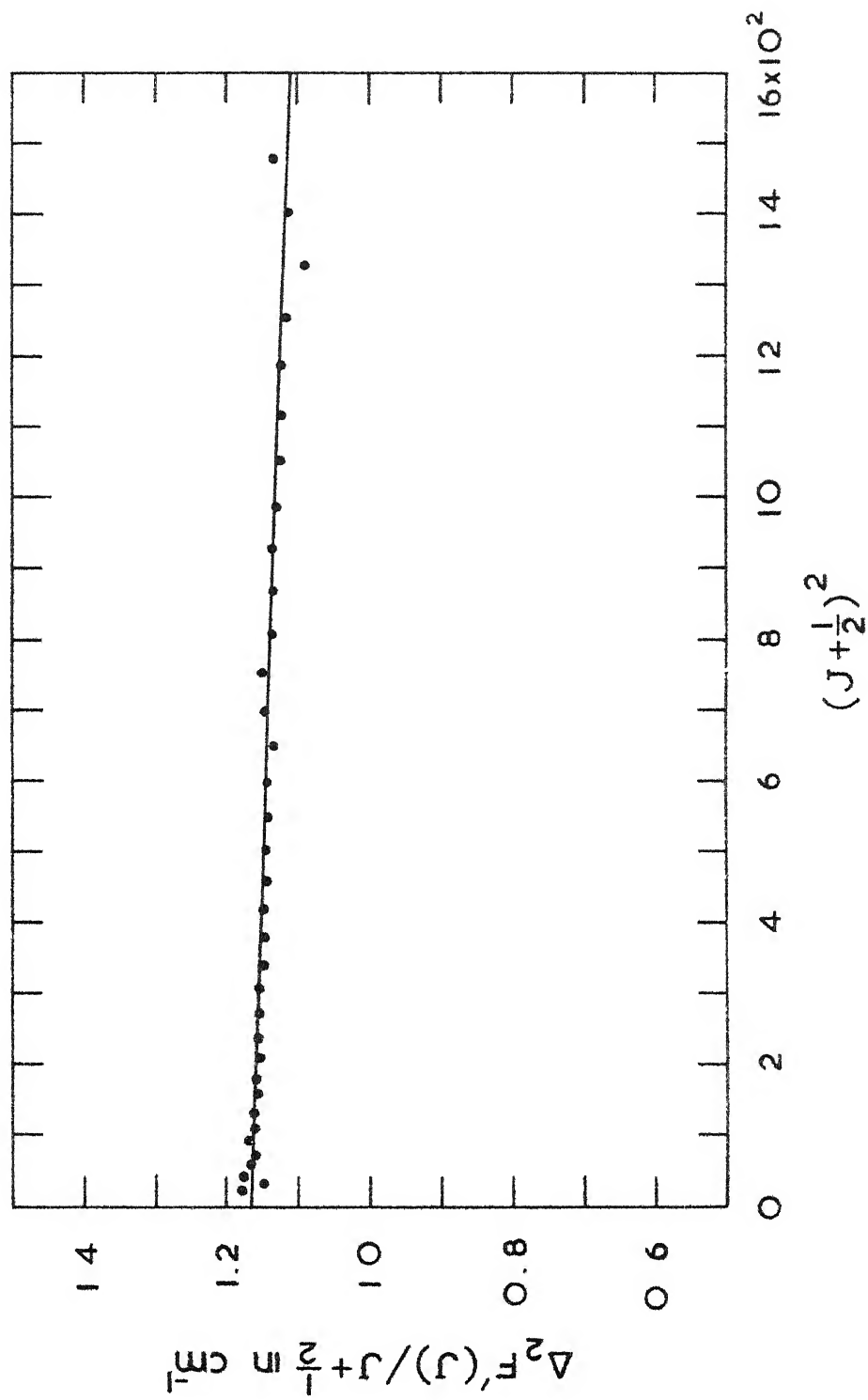
Fig.I.5 - GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS AND CHECKING OF J NUMBERING for $v'=2$ in F_1-F_1 sub-band of $Se^{80}O$
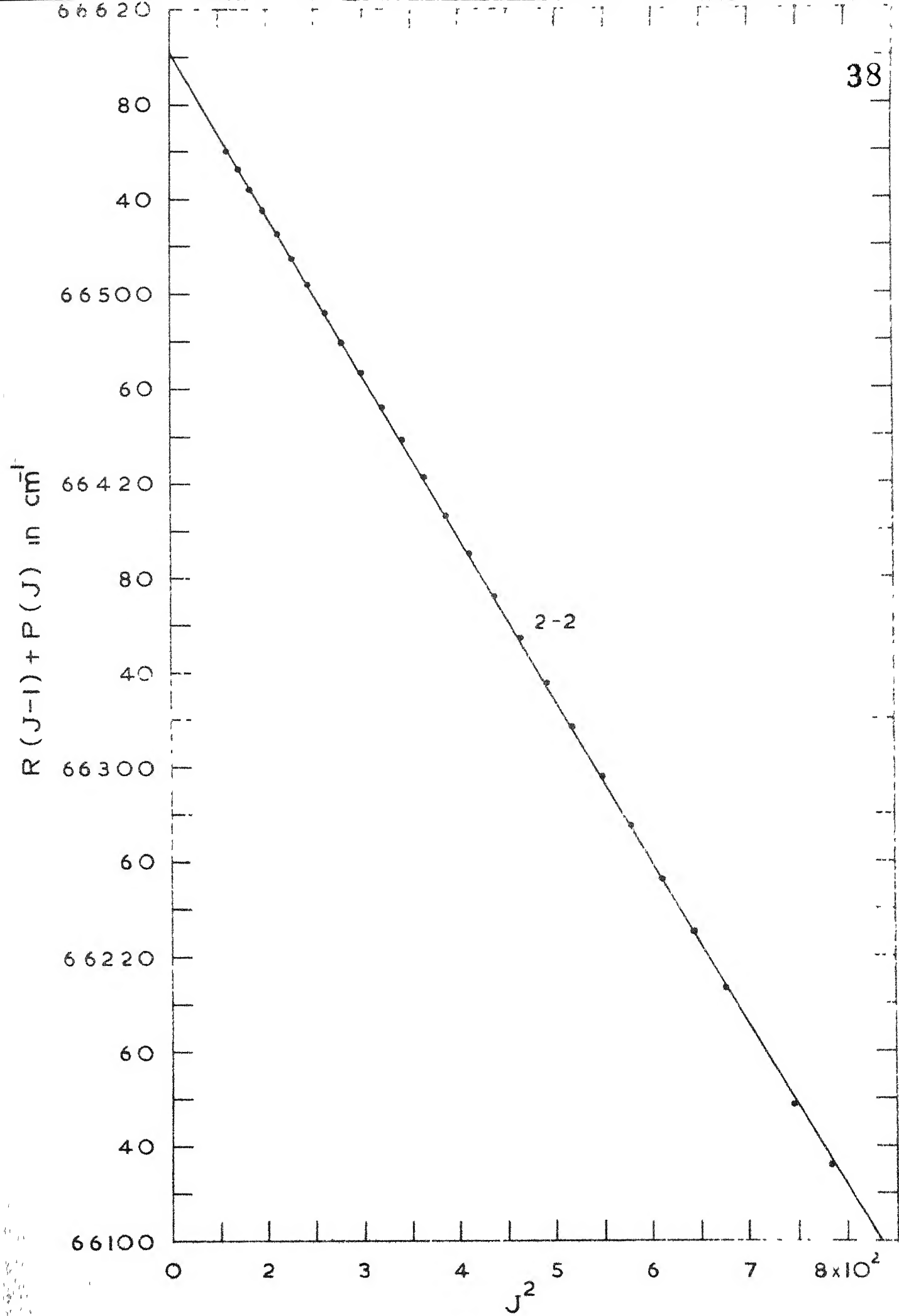
Fig I 6(a)-GRAPHICAL DETERMINATION OF BAND ORIGIN
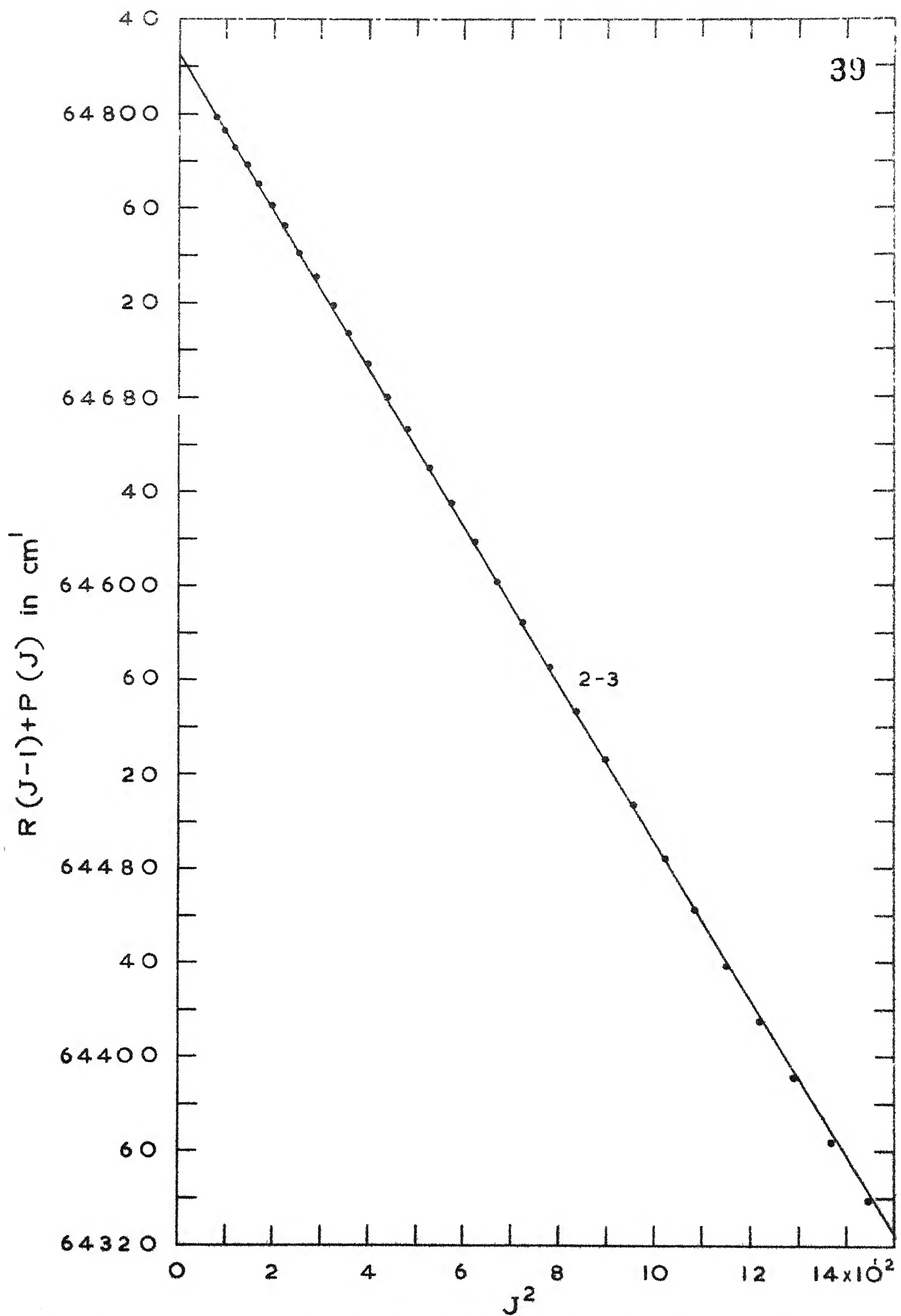
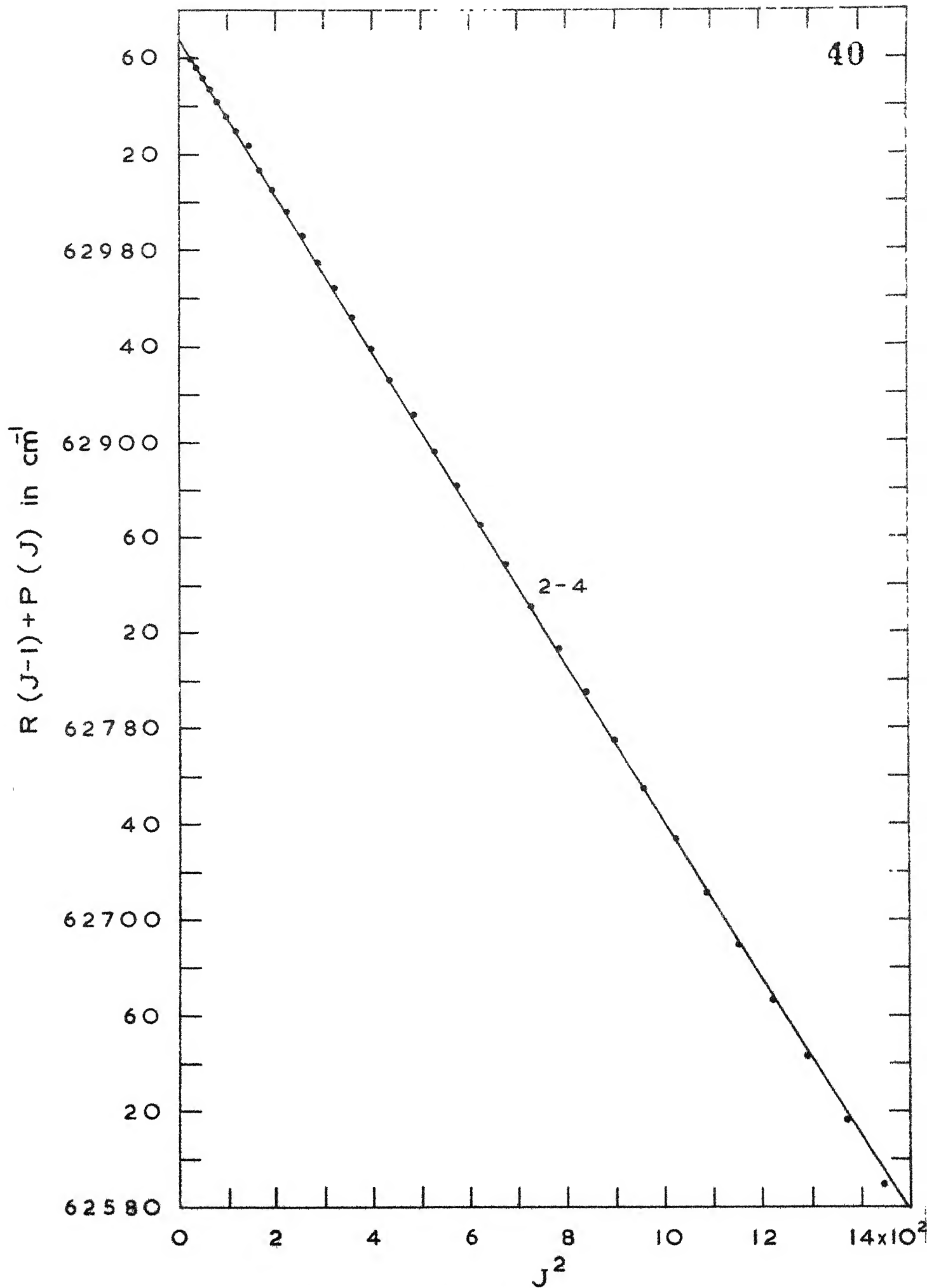Fig.I.6(b) - GRAPHICAL DETERMINATION OF BAND ORIGIN

Fig.I.6(c) - GRAPHICAL DETERMINATION OF BAND ORIGIN
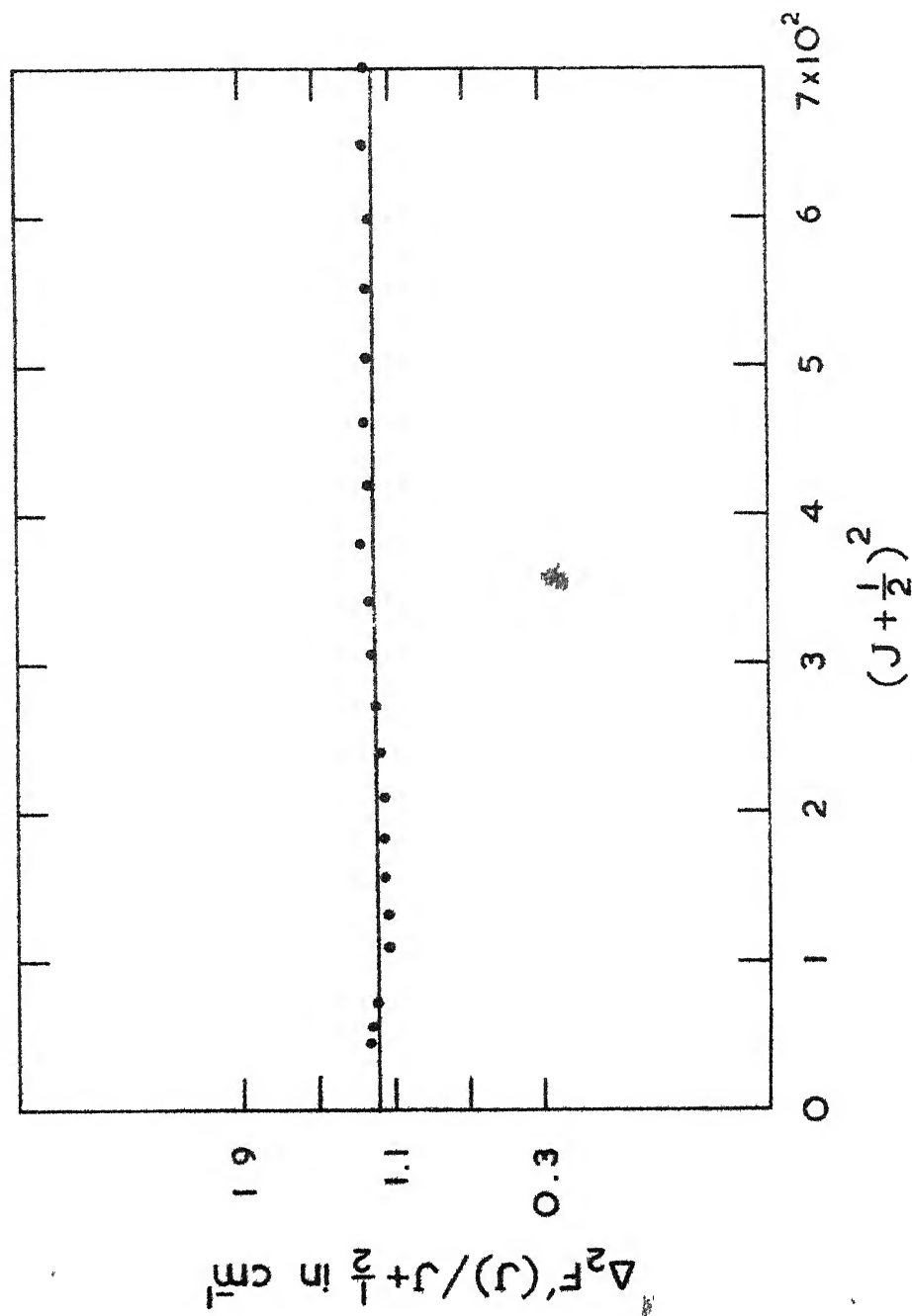
Fig.I.7- GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS AND CHECKING OF J NUMBERING for $v'=2$ in $F_2^- F_2^-$ sub-band of $Se^{80}O$
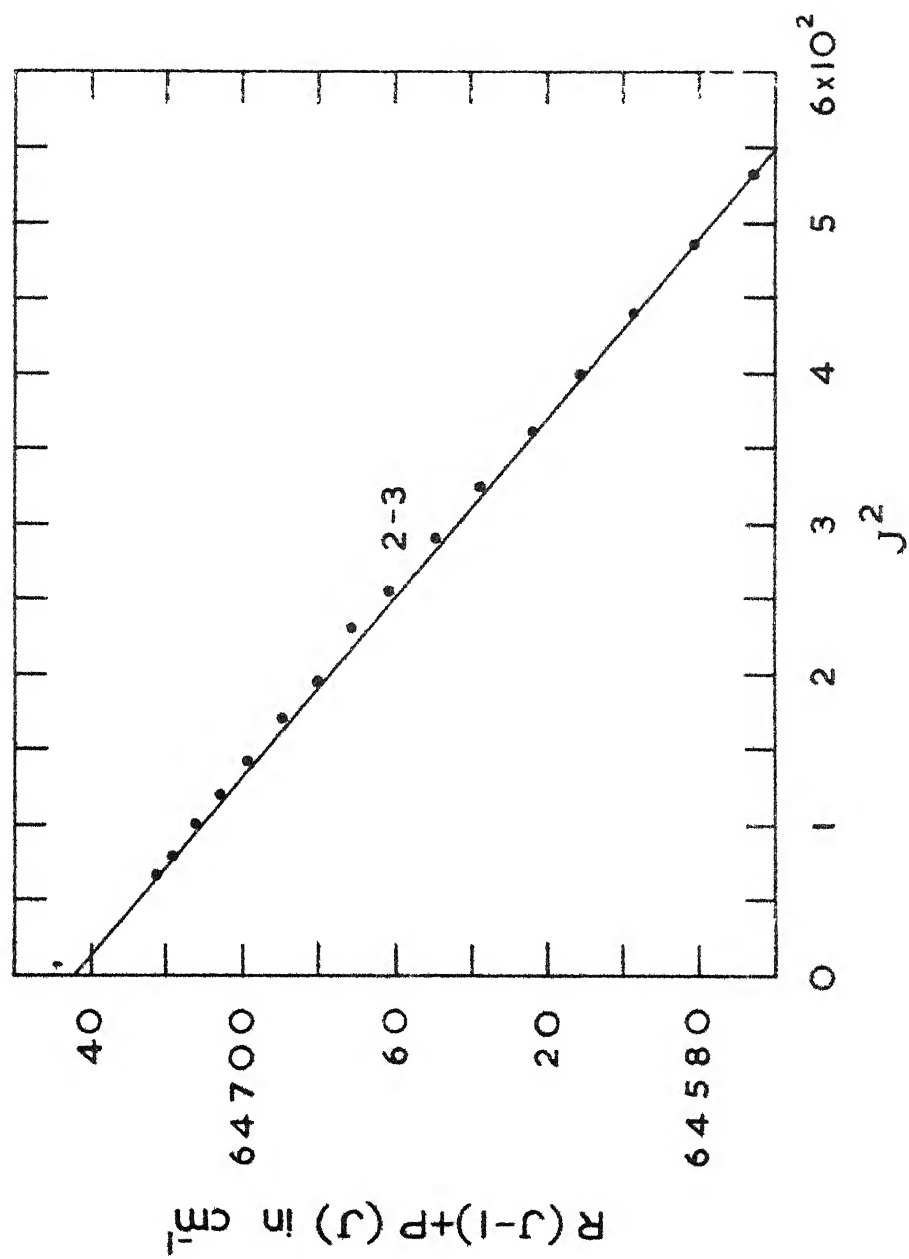
Fig.I.8(a) - GRAPHICAL DETERMINATION OF BAND ORIGIN
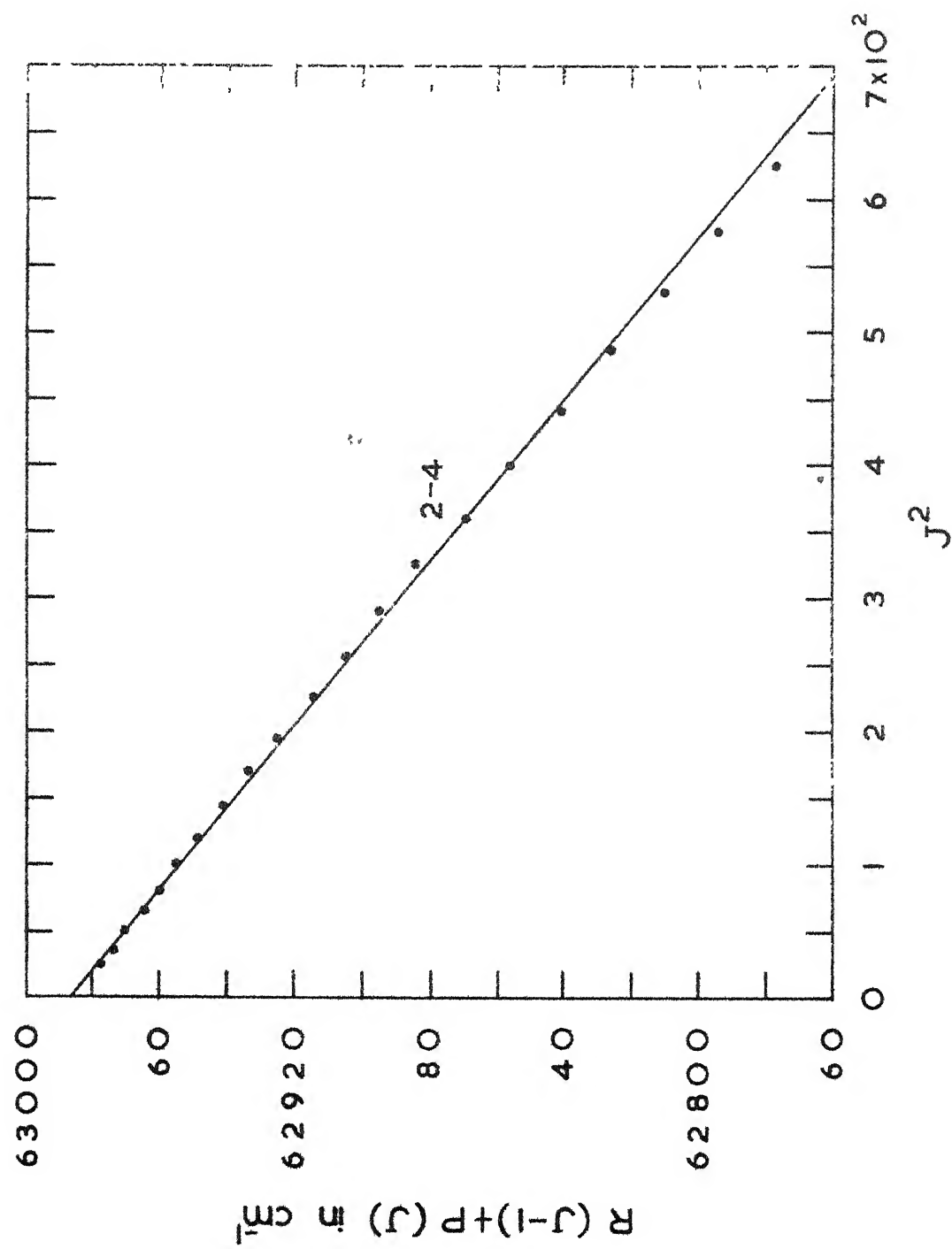
Fig.I.8(b)-GRAPHICAL DETERMINATION OF BAND ORIGIN

CHAPTER II

SO CALLED "SeN" BANDS

ABSTRACT

The combination of selenium and nitrogen in a sealed quartz discharge tube and excitation by a microwave oscillator gave certain new bands in the region $3960\mathring{A}$ – $5675\mathring{A}$. The bands could be arranged into two systems assuming the emitter to be SeN. By using separated isotopes of selenium, it is proved, however, that Selenium is not involved in the emission of the above bands. High resolution spectra of some of the prominent bands are photographed and features of two of the bands are described. No definite conclusions could be arrived at, about the emitter.

INTRODUCTION

Diatomic molecular species obtained from combinations of Vth group and VIth group elements have been extensively studied spectroscopically. Such intercombinations are known for oxygen and sulphur with nitrogen and phosphorus (Herzberg, 1950). However, no such combination is known with selenium. With the exhaustive work on NO and NS molecules known, it was thought worthwhile to explore whether or not a combination of selenium and nitrogen is possible, if so under what conditions. what sort of molecular formation takes place and subsequently how the electronic spectra would look. As has been already stated in Chapter I, work on SeN molecule was attempted in a general programme of spectroscopic work on selenium compounds, SeO and SeN. By the time the investigation was in progress, Guy Pannetier and others (1965) reported a group of bands attributable to NSe radical obtained in an electrical discharge of nitrogen and Se Cl_4. The same group of bands along with additional bands are obtained in this investigation by combining selenium and nitrogen in a sealed quartz discharge tube. The details of the experimental work to excite the new bands and a discussion on the nature of the emitter by using separated isotopes of selenium are given in this Chapter. High resolution spectra of some of the new bands have been photographed and features of two of the bands are discussed. The conclusions arrived at, on the emitter are also given at the end of the Chapter.

EXPERIMENTAL

The new spectrum was excited by a direct combination of selenium and nitrogen gas in a sealed quartz discharge tube. The natural selenium sample used was from British Drug Houses, whose purity was quoted to be 99.5%. Nitrogen was used from a high pressure cylinder through a liquid nitrogen trap. Not all the tubes sealed by the above procedure gave the new spectrum. It was found that by sealing a number of tubes with various amounts of selenium sample at varying pressures of nitrogen, a few tubes were successfully operative. In other words, critical amounts of sample of selenium and nitrogen gas were required to excite the new spectrum. It was found that these critical amounts of samples, varied with the length of discharge tube. Keeping the length of the discharge tube fixed in all the trials, it was not very difficult to seal a successful tube after about three or four attempts. The life of the sealed tube was found to be about 50 hours with intermittent operation.

The discharge tube thus sealed, was excited by the microwave oscillator. At first, with about 10% of the total power, nitrogen gas in the sealed tube was excited with the help of tesla discharge. Now by slowly increasing the power to about 50%, selenium started vapourizing and showing its own spectrum, suppressing the nitrogen spectrum. At this stage, the power was slowly reduced to about 25% where a new colour of discharge

could be seen developing and it was checked with the help of a
hand spectroscope that neither the spectrum of nitrogen nor the
spectrum of selenium was present under these conditions. Howe-
ver, if the power was reduced to 10% again, the colour of the
discharge became reddish showing the presence of nitrogen. In
a similar manner, when the power was increased the selenium
spectrum alone could be seen. Thus it was found that not only
the length of the discharge tube, amounts of selenium and nitro-
gen gas introduced but even the amount of power required for
excitation also was critical to obtain the new spectrum.

From what has been said above, it would have been diff-
icult to stabilize the conditions in a conventional discharge
tube. Selenium vapour has the nature of settling on the colder
portions of the walls of the discharge tube when heated at one
place and it will be very difficult to get a combination of the
selenium vapour and nitrogen gas in a discharge tube. The cri-
ticality of the conditions was found to be the reason that it
could not be stabilized by any other means. So, the sealed tube
technique proved to be very convenient in this particular case,
apart from the advantages which are discussed in Chapter I(a).

In the initial stages, the spectrum was recorded on a
3-prism small glass spectrograph, which has a dispersion of about
28 Å/mm at about 4500Å. It was also necessary to take various
spectra with different times of exposure, on a 3.4 meter Jaco

grating spectrograph in the first order at a dispersion of 2.5$\overset{\circ}{A}$/mm using a 4" grating (30,000 lpi) blazed for 4,000$\overset{\circ}{A}$. Throughout the work Ilford R-40 plates were used for recording the spectra. The iron arc was used as a standard for wavelength calibrations.

The plates were measured on a Zeiss Abbe comparator. The comparator readings were directly fed to the IBM computer and the vacuum wavenumbers of the band heads were obtained by using a standard programme in which Edlen's vacuum correction formula is incorporated. The accuracy of the measurements for the band heads was found to be $\pm$ 2cm^{-1} for the bands photographed on the prism spectrograph and $\pm$ 0.5cm^{-1} on Jaco spectrograph.

Description of the Spectrum:

The present investigation revealed about 50 bands in the region 3960$\overset{\circ}{A}$ - 5675$\overset{\circ}{A}$. All the bands are single headed and degraded to longer wavelengths. The bands include all the 30 bands reported by Guy Pannetier and others (1965). However, the extra bands observed in the same region with similar structure could not be fitted with his analysis. The band head data is given below and the eye estimated intensities are marked in the paranthesis.

25226(4)	24895(4)	24527(5)	24386(2)	24237(5)	23913(5)
23773(2)	23679(2)	23595(3)	23436(7)	23303(8)	23256(6)
23045(3)	22981(10)	22848(9)	22818(9)	22523(3)	22502(9)

22457(9) 22325(10) 22132(6) 22060(10) 21932(10) 21891(10)

21770(7) 21583(6) 21400(9) 21014(7) 20967(9) 20862(9)

20728(3) 20616(3) 20573(6) 20493(9) 20257(2) 20060(7)

19959(3) 19899(3) 19767(5) 19591(9) 19463(9) 19363(9)

19161(9) 18885(9) 18700(10) 18481(10) 18277(10) 18015(9)

17820(9) 17613(9).

Nature of the expected SeN spectrum:

The nearest isoelectronic molecules of SeN are GeF and AsO. GeF (μ= 15.0627) has a ground state frequency of 665.0cm^{-1} and AsO (μ= 13.1848) has 967.4cm^{-1}. SeN whose reduced mass is 11.97 is expected to have still larger ground state vibrational frequency. If one considers similar molecules to NSe i.e., NO and NS, the ground state vibrational frequencies are 1903cm^{-1} and 1220cm^{-1} respectively and the frequency for SeN should be still less. From the above considerations, it was estimated that ground state vibrational frequency for SeN to be about 1000cm^{-1}. The isoelectronic molecules and similar molecules to SeN have $^2\pi_r$ (Hund's case(a)) as their ground state. The spin-orbit coupling strength in the ground state in GeF was found to be 930cm^{-1} and that in AsO to be 1027cm^{-1}. In NO and NS, it is known that the spin-orbit coupling strength is 121.0cm^{-1} and 223.0cm^{-1} respectively. In SeN, one can expect that this value may be of the order of that found in GeF and AsO. Any analysis of SeN spectrum should incorporate the above considerations on vibrational

frequencies and the spin-orbit coupling values, for a consistency. To this extent, the analysis of Guy Pannetier and others (1965) needs revision. All the bands observed by them were attributed to be probably arising from a single system, the upper and the lower state beloning to Hund's case(a) type of coupling.

A new analysis of the spectrum obtained with natural selenium incorporating the above arguments is attempted assuming the emitter to be SeN. Most of the bands could be analysed as $^2\Sigma - X^2\pi_r$ and $^2\Delta$ or $^2\pi - X^2\pi_r$ the positions of the excited states being estimated at 30,420cm^{-1} and 29,980cm^{-1}, $^{29955cm^{-1}}$ respectively. The lower state of these transitions is assumed as the ground state. The vibrational frequency of this state was about 1000cm^{-1} and the separation of the $^2\pi$ components in the ground state came out to be 980 cm^{-1}.

In this analysis the bands at

v"+0	v"+1	v"+2	v"+3	v"+4	v"+5	v"+6	v"+7
22818	21891	20967	20060	19161	18277	–	–
23773	22848	21932	21014	–	–	–	–
23436	22502	21583	–	19767	18885	18015	–
24386	–	22523	–	20728	–	–	–

form the v'=0 and v'=1 progressions of the $^2\Delta$ or $^2\pi - X^2\pi_r$ and
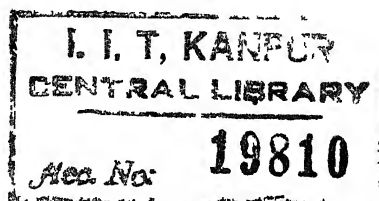
v"+0	v"+1	v"+2	v"+3	v"+4	v"+5	v"+6	v"+7
23256	22325	21400	20493	19591	18700	17820	-
24237	23303	-	-	20573	-	-	-
23913	22981	22060	-	20257	19363	18481	17610
24895	-	23045	22132	-	-	19463	-

form the $v'=0$ and $v'=1$ progressions of the proposed $^2\Sigma - X\,^2\pi_r$. Also such an analysis is probably consistent with the expected molecular states. The pronounced progressions are marked in Fig. II.1.

The ground state for SeN which has 41 electrons can be written with the usual nomenclature of Mulliken (1932) as
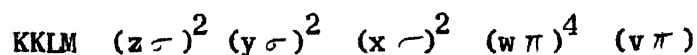
$$KKLM \quad (z\sigma)^2 \; (y\sigma)^2 \; (x\sigma)^2 \; (w\pi)^4 \; (v\pi)$$

which gives the ground state as $^2\pi_r$ similar to NO, NS, GeF and AsO whose ground states are established to be $^2\pi_r$. The first few excited state electronic configurations and the states obtained thereby are the following

1. $KKLM \quad (z\sigma)^2 \; (y\sigma)^2 \; (x\sigma)^2 \; (w\pi)^3 \; (v\pi)^2 : {}^4\pi, \; {}^2\pi(3) \; \text{and} \; {}^2\phi$

2. $KKLM \quad (z\sigma)^2 \; (y\sigma)^2 \; (x\sigma) \; (w\pi)^4 \; (v\pi)^2 : {}^4\Sigma^-, \; {}^2\Sigma^+ \; {}^2\Sigma^- \; \text{and} \; {}^2\Delta$

The excited states of the proposed systems could be generated from the above given configurations.

Further experimental evidence supporting that the emission may be due to SeN is the following:

A) The initial stages of the discharge with less power from the microwave oscillator show only N_2 first and 2nd positive bands. This suggests selenium has not gone into vapour state in the sealed tube. As one increases slowly the power in the oscillator the selenium metal goes into vapour state and the new emission attributable to SeN is seen supressing the original N_2 emission. If the power is still increased even the new emission is suppessed and bands due to Se_2 dominate in the same region. Therefore depending on the amount of selenium vapour present in the sealed tube one could have emission due to N_2 or due to SeN or due to Se_2 in the same region 3960Å-5675Å. It is believed, when the new emission is observed, that selenium and nitrogen are in appropriate proportions so as to form SeN molecule and this is discussed already in the experimental section of this Chapter.

B) When the new emission is recorded, photographs clearly show three atomic lines at 4730Å, 4739Å, 4742Å (shown in Fig.II.1) which are identified as selenium atomic lines. In the ultraviolet side of the new emission there are some violet degraded bands whose heads were measured and found to be due to nitrogen second positive system. Similarly on the long wavelength side also some close violet degraded bands were identified and it was found that they belong to nitrogen first positive system. These facts also

tell that only selenium and nitrogen emissions are present in
the discharge and as the new emission does not belong to either
of them, it would be preferred to conclude that the emitter is
SeN in the absence of any further information either on detailed
high resolution work and/or the use of separated isotopes.

Emissions using separated isotopes of selenium:

Using separated isotopes of selenium (95% enriched)
obtained from Oak Ridge National Laboratories, USA the experi-
ments were repeated. For comparison the spectrograms from
natural selenium, Se^{78}, Se^{80} are shown in Fig.II.1. It is evi-
dent from the figure that the spectra using natural selenium
sample and isotopic enriched selenium in the sealed tubes are
identical. There is no shift of any nature in the positions
of band heads from separated isotopes. In other words, the
spectra using enriched selenium show the same heads as from
natural sample and the emission from both isotopes yields iden-
tical spectra. Thus, one is forced to infer that this observed
new emission is not resulting from a molecule involving selenium
as at least one of the constituents.

High Resolution Spectra:

The short wavelength end of the spectrum is photographed
in the second order of a 22 ft. grating spectrograph at a disper-
sion of $0.6\text{Å}/mm$ and the longer wavelength end bands were recorded
in the second order of a 3.4 meter Hilger grating spectrograph,

using a grating blazed for 10,000Å, at a dispersion of about 1.0Å/mm.
This part of the work was done at BARC, spectroscopy division, Bombay.
When the spectra were taken with natural sample of selenium as well
as with enriched samples of selenium it was found that there was
line to line correspondence thus conclusively showing the absence
of selenium in the emitter.

The bands identified as belonging to the same progression
in the proposed vibrational analysis do not show the same structure.
Even the bands that are not overlapped show divergent structures.
The high resolution spectrum of bands at $20060cm^{-1}$ and $20493cm^{-1}$ is
shown in Fig.II.2. These two bands according to the proposed ana-
lysis belong to two different systems. A brief description of the
features of both the bands is given below:

$20060cm^{-1}$ Band:

This band consists of a strong branch which looks like a
Q branch starting right from the head and proceeds towards the
longer wavelength side. It can be seen that a little away from the
head there is a splitting of the branch into two separate lines whose
intensities are exchanged through a maximum and the splitting also
was found to be maximum at the same place. After a certain distance
the splitting collapses into one single line and the intensity of
the branch as such starts decreasing slowly. Part of these features
are shown in the Fig.II.2. Also, one can see that a weak branch
starts almost nearer the head and continues to go towards the longer

wavelength side frequently crossing the intense branch. In this branch also the splitting of the line is observed and it has similar features as that of the intense branch. Nothing could be decided either about the transition in the absence of another band with similar structure. In fact, there were no two bands for which there is a similar structure.so that an attempt for an analysis could be made.

$20493cm^{-1}$ Band:

This band showed quite a complex structure at the head and as one moves away from the head one can find that a group of four lines move parallel to each other. The distance between the first two lines was larger than the distance between the latter two lines in the same group. From the appearance it looks that they are P and R branches running parallel to each other. However, nothing more could be said about this band because of the absence of further information. The above said features are marked in Fig.II.2.

Conclusions:

In conclusion it is felt that the emitter of this group of bands is not SeN. Also this cannot be new set of bands from Se_2 as is verified from the isotope shift considerations. One could also rule out ~~nitrogen~~ N_2 as the emitter as the high resolution plates do not show any alteration of intensity of the rotational lines because the spin of nitrogen nucleus is one and should reflect in the rotational structure.

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²Δ or ²Π–X²Π

²Σ–X²Π

v' = 1
v' = 0

v' = 0
v' = 1

18015
18277
18885
19161
19767
20060
20725
20967
21014
21583
21691
21932
22502
22537
22818
22845
23436
23713

17820
18481
18700
19363
19463
19591
20257
20493
20573
21400
22060
22132
22325
22981
23045
23256
23303
23913

4730 78A
4739 03A
4742 25A } Se Lines

⁷⁸SeN
SeN
⁸⁰SeN
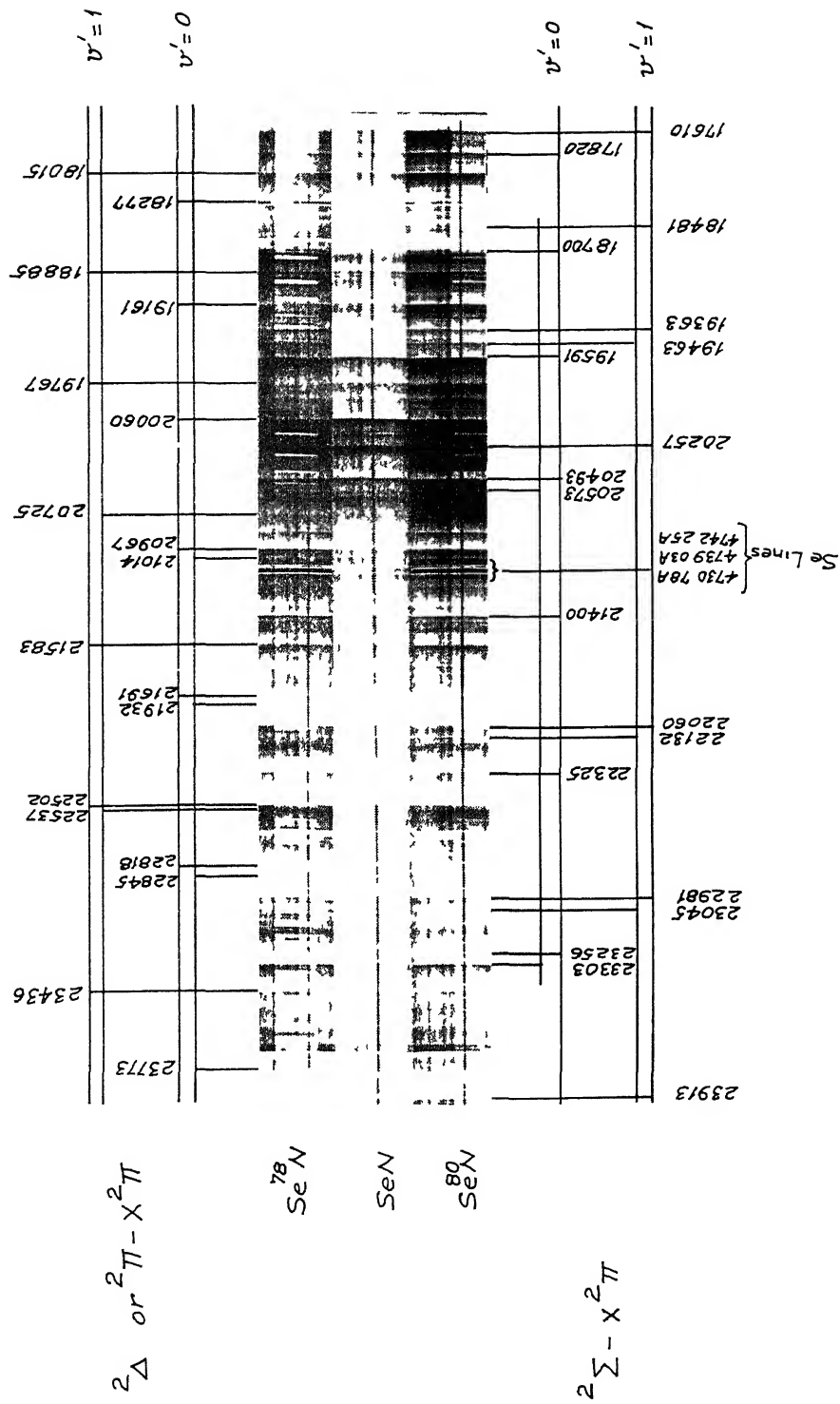
Fig II 1 Photograph of "SeN" taken on Zeiss 3-Prism glass spectrograph at a dispersion of about 28 Å/mm, with separated isotopes of selenium, showing prominent progressions of the proposed analysis

5017 255

4985 385

(a)

4905 083

4878 733

(b)
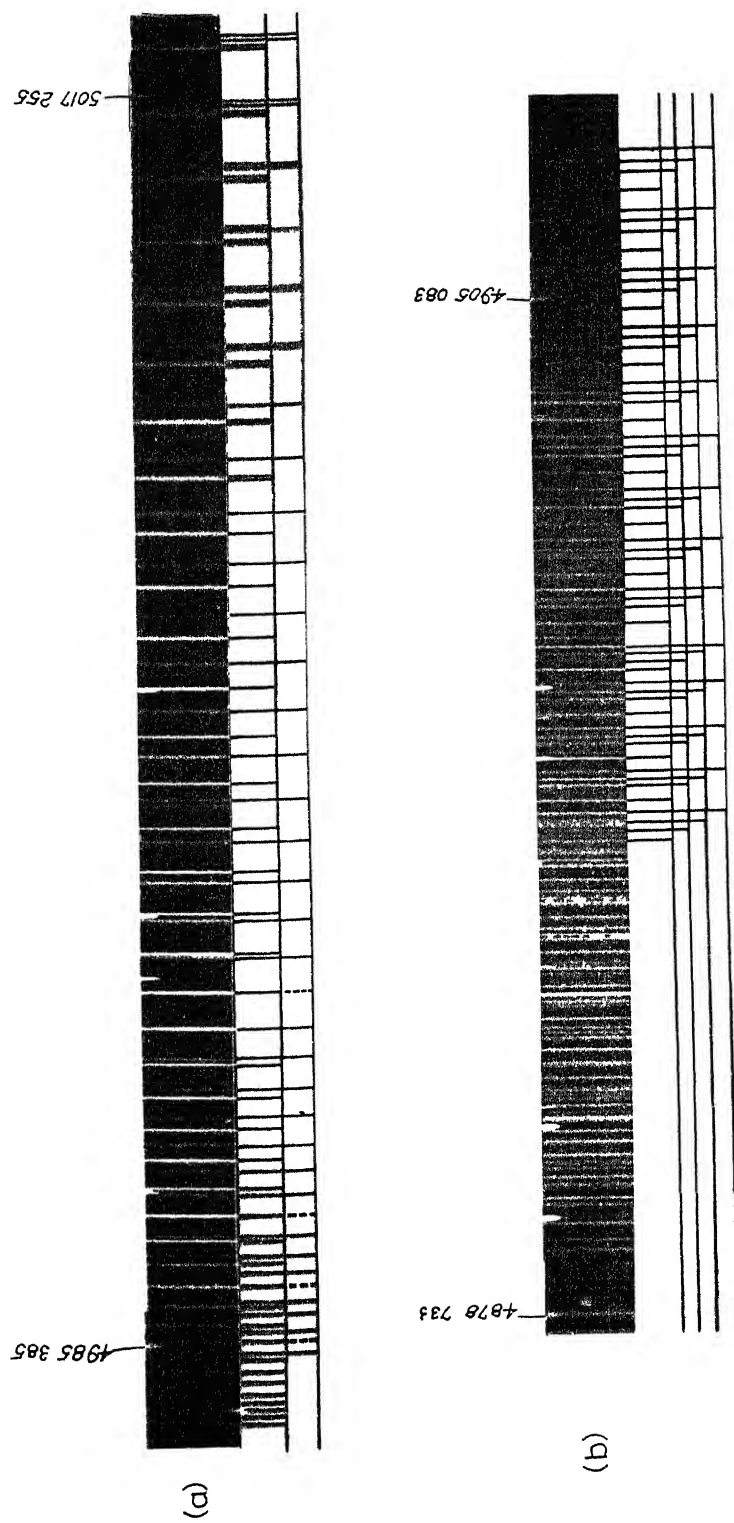
Fig II 2 Rotational Structure of two bands of "Se N" photographed in the II order of a 3 4 m grating Spectrograph at a dispersion of 1 1 Å/mm (a) band at 20060 cm^{-1}

(b) band at 20493 cm^{-1}

CHAPTER III

ROTATIONAL ANALYSIS OF Te_2^{128} MOLECULE

ABSTRACT

The high resolution spectrum of Te_2^{128} molecule is photographed by exciting the sealed tube with a microwave oscillator. Rotational analysis is carried out for six bands belonging to the $v'' = 0$ progression and the constants of the ground and excited states are obtained for the first time. A brief discussion is made on the observed perturbation and a comparison is made with the known constants of Te_2^{130} molecule,

INTRODUCTION

The study of the spectra of Te_2 molecule in the near ultraviolet region has been the subject of numerous investigations. Yet no consistent vibrational analysis and rotational analysis of the bands were known till very recently. With the availability of separated isotopes of Tellurium, it has been possible to excite the spectrum of Te_2 molecule in this laboratory, in a sealed quartz discharge tube by Jha (1968). He revised the existing vibrational analysis of the near ultra-violet bands and proved from the expected isotopic shift considerations that the vibrational numbering given by Olsson(19 38) is the correct one. It was also found by him that a kind of perturbation exists for all the bands with $v \geqslant 19$ in the upper state. Rotational analysis of six bands was done and the rotational constants for the ground and excited state were evaluated by him for Te_2^{130} molecule for the first time showing the transition to be $^1\Pi_u - ^1\Sigma_g^+$ type.

This investigation on Te_2^{128} molecule was taken up to find whether the analysis of the bands at $v' = 18$ and 19, where the perturbation is supposed to start, would yield additional information about the nature of the perturbation. More so, it was felt that it would be possible to confirm the already existing results on Te_2^{130}.

In this Chapter, the details of the results obtained from the rotational analysis of six-bands of $v''=0$ progression of Te_2^{128} in the region $3000\text{Å} - 4000\text{Å}$ are given and a comparison is made with the results calculated from Te_2^{130}.

EXPERIMENTAL

Small samples of Te^{128} enriched to 95% obtained from Oak Ridge National Laboratories, USA were sealed in a quartz tube 5 to 6cm long and about 9mm diameter. The sealing was done in a similar manner as described in the experimental section of Chapter I(A). However, in this case Argon at a pressure of 5 to 6mm was filled as a preexciting material for the sealed quartz discharge tube which was excited by the microwave oscillator. Since Tellurium vapour is formed at $900^\circ C$ or above, it was necessary to heat the quartz tube externally by a laboratory built furnace constantly, to maintain the discharge of Tellurium, while 50% of the microwave power was fed as shown in Fig.I.2. An emarald greenish discharge indicated the excitation of Te_2^{128} spectrum which could be checked with the help of a hand spectroscope by the presence of very closely spaced and red degraded bands in the visible region.

The spectrum excited under the above experimental conditions was recorded in the region $3000\overset{o}{A} - 4000\overset{o}{A}$ on a 3.4 meter Jaco grating spectrograph in the IIIrd order of a 4" grating (30,000 lpi) blazed for $10,000\overset{o}{A}$, at a dispersion of about $0.6\overset{o}{A}/mm$. Kodak 103a-0 type plates were employed and the exposure timings varied from 2 to 4 hours. Iron arc was used for calibration purposes. The measurements were done on a Zeiss Abbe comparator and the vacuum wavenumbers of all the rotational lines were obtained on an IBM computer using Edlen's vacuum correction formula. The accuracy of the

measurements was found to be $\pm 0.02 cm^{-1}$ for sharp rotational lines and $\pm 0.04 cm^{-1}$ for the broad rotational lines.

ROTATIONAL ANALYSIS

All the bands belonging to the $v'' = 0$ progression were red degraded and single headed. Each band showed two branches running parallel to each other indicating that they are the P and R branches. It was rather easy to decide which one of them is R and P. Another feature of the bands was that it was found both R and P branches start coming closer, merge together in one of the bands and get separated again as one moves from the long wavelength end bands to the short wavelength side. These features are shown in Figs.III.1 and III.2.

Once the branches are picked up, in any rotational analysis it is necessary to look for common properties between the bands to arrive at certain conclusions about the molecule under investigation. Since it is known that all six bands recorded belong to $v'' = 0$ progression it is natural to form the combination differences for the ground state for each band and compare. Such ground state combination differences are govented by the expression given below:

$$\Delta_2 F'' = R(J-1) - P(J+1) = (4B_v'' - 6D_v'') (J+\tfrac{1}{2}) - 8D_v'' (J+\tfrac{1}{2})^3$$

$$...III.1$$

where the symbols have the usual meaning.

Since the exact numbering of all the rotational lines is not yet known, at this stage one could obtain various sets of combination differences for an arbitary running number J. However, the correct set of combination differences was chosen from a least squares calculation as was done in Chapter I.B. After this is done, an average of the $\Delta_2 F''(J)$ values from all the bands is taken and a graph was drawn against a running number J. A straight line graph was obtained and the adjustment of the abscissa axis was done till the line intersects the abscissa at $J = -\frac{1}{2}$. Giving a consecutive number of J, it was found that the estimated rotational constant was coming too high to belong to such a heavy molecule like Te_2. At this stage, help was taken from the following two points:

i) The observed rotational structure showed that the transition is most probably of $^1\Sigma_1^- {}^1\Sigma_1^-$ type since no doubling of the rotational lines was observed even for the lines involving high J value thus indicating the absence of a multiplet nature.

ii) It is known a priori that $^{54}Te^{128}$ is an even-even nucleus, hence has a nuclear spin value zero and such molecules should lead to a situation in the rotational structure that alternate rotational lines should be missing in each branch in a $\Sigma_1^- \Sigma_1$ type transition. However, a correct J numbering was fixed by drawing a graph of $\Delta_2 F''(J)/(J+\frac{1}{2})$ vs $(J+\frac{1}{2})^2$ and the graph is shown in Fig.III.3. It was found that only even numbers of J values exist for the lower state. The vacuum wavenumbers of all the rotational lines in R and P branches after fixing the correct J numbering are given in Table III.1 for three bands (15-0), (16-0) and (17-0) and in Table III.2

for the other three bands (18-0), (20-0) and (21-0). The set of combination differences for the ground state after fixing the correct J numbering is shown in Table III.3. It was found from the analysis of (19-0) band that only lines with very high J values exist. The wavenumbers and combination differences are presented in Table III.4(a) and (b) respectively. However, the values for (19-0) band may not be reliable because of extrapolation from very high J values. (In all the tables of wavenumber data and combination differences, at the places marked (-) it has not been possible to locate the rotational lines because of overlapping by atomic lines. Also, wherever the value of combination difference is much off from the average values, it was found that it is due to broad rotational lines and/or measurement error).

Since it is seen that alternate rotational lines are missing, the quantities $R(J)+P(J)$ are formed and a graph is drawn vs $J(J+1)$ to find the band origins for the six bands and the values of $(B_v' - B_v'')$ are also derived from the same graphs. This method of finding the band origins is necessary because the alternate rotational lines were found to be missing. The following expression

$$R(J)+P(J) = 2(\nu_0 +B_v') + 2(B_v'-B_v'') J(J+1) \quad \ldots \quad III.2$$

is formed in order to obtain the band origin value and the values of $(B_v'-B_v'')$. A graph is drawn for $R(J) + P(J)$ vs $J(J+1)$, the intercept giving the band origin value and the slope $(B_v'-B_v'')$. The values from these graphs are tabulated in Table III.5(a). The graphs are shown for all the six bands in Figs.III.4 and III.5.

The rotational constants were obtained for all the six vibrational levels in the upper state and the results thus obtained are tabulated in Table III.5(b) alongwith the rotational constant B_0". Since there are six bands for which the rotational constants in the upper state are obtained, it has been possible to get B_e and α_e values for the upper electronic state from the following relation.

$$B_v = B_e - \alpha_e \; (v+\tfrac{1}{2}) \qquad\qquad \text{.... III.3}$$

α_e is a constant and usually positive and much smaller than B_e, the rotational constant corresponding to the equilibrium internuclear distance r_e.

However, a check for all the constants obtained from graphical method could be made by feeding the vacuum wavenumber data to an IBM - 7044 computer incorporating a least squares fit programme and the agreement for the band origin and the rotational constants was found to be excellent. All the above observations as expected support the assigned transition as $0_u^+ - 0_g^+$ (in case (c) approximation) for Te_2^{130} by Jha and Ramachandra Rao(1969).

DISCUSSION

As can be seen from Figs.III.1 and III.2, the structure of the P and R branches is rather clear. It was not possible to follow up the 19-0 band and it showed a complex line like structure and this band happens to be the one where the perturbation is

supposed to have set in. One can notice some of the rotational lines of this band with very high J values ⌐verlapping the structure of 18-0 band (Fig.III.2). The computed B value from the graph for 19-0 band does not deviate from the general formula of the upper state B values but the band origin was found to be displaced from its expected position. These features continue to be there in 20-0 and 21-0 bands also. It is surprising that the B values did not deviate from the general formula for bands $v' \geqslant 19$ though the bands are shifted as a whole from about $v' = 19$ which can be attributed to a homogeneous perturbation ($\Delta \Lambda = 0$). In fact the perturbation may really be starting somewhere from $18 < v < 19$ and the only conclusion is that a similar state is the one which is responsible for this kind of perturbation.

With the availability of rotational constants and band origin data for Te_2^{128} it should now be possible to check and confirm the results of Jha and Ramachandra Rao(1968). The isotopic shift obtained from the band origin data for all the seven bands of Te_2^{128} and Te_2^{130} is presented in Table III.6(a) and the values agree closely to those obtained from the formula for the band head data, thus indicating the validity of the numbering for $v'' < 19$. The rotational constants of two isotopic molecules differ and they are related in the following way:

$$B_e^i = \rho^2 B_e \text{ and } \alpha_i^e = \rho^3 \alpha_e \qquad \dots \text{ III.4}$$

where B_e^i and α_e^i correspond to the constants of the isotopic

molecule and B_e and χ_e to the normal molecule and ρ is the ratio of the reduced masses of isotopic to the normal molecules, taken in that order. The B_e' and χ_e' of Te_2^{128} obtained from the present analysis are compared with those values expected from the existing results on Te_2^{130} and a comparison is shown in Table III.6(b). It also contains the obtained and expected values of B_o''. As one can see, the agreement is good for all the constants obtained from the present analysis.

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Table III.1 - Wavenumbers of Rotational Lines for Te$_2^{128}$

J	15-0 R(J)	15-0 P(J)	16-0 R(J)	16-0 P(J)	17-0 R(J)	17-0 P(J)
8		24464.45				
10		63.95	24605.75			
12		63.48	05.33			24741.39
14	24464.60	62.81	04.99	24603.28	24742.99	41.25
16	64.11	62.08	04.52	02.54	42.50	40.54
18	63.62	61.34	03.92	01.76	41.89	39.72
20	62.97	60.49	03.39	00.88	41.25	38.82
22	62.33	59.54	02.74	24599.74	40.54	37.86
24	61.60	58.59	01.91	98.90	39.72	36.80
26	60.77	57.52	01.05	97.81	38.92	35.69
28	59.91	56.40	24599.92	96.62	37.98	34.48
30	58.92	55.22	99.14	95.39	36.94	33.22
32	57.89	53.90	98.05	94.00	35.83	31.87
34	56.73	52.57	96.89	92.61	34.66	30.44
36	55.56	51.15	95.66	91.15	33.30	28.96
38	54.33	49.63	94.29	89.64	32.03	27.33
40	53.00	48.06	92.88	88.00	30.63	25.67
42	51.58	46.41	91.49	86.27	29.13	23.95
44	50.11	44.66	89.98	84.49	27.54	22.10
46	48.51	42.87	88.34	82.59	25.88	20.20
48	46.88	40.96	86.59	80.65	24.15	18.24
50	45.17	39.01	84.85	78.63	22.34	16.18
52	43.39	37.00	83.01	76.60	20.45	14.05
54	41.53	34.87	81.05	74.39	18.49	11.82
56	39.57	32.70	79.08	72.12	16.42	09.54
58	37.56	30.40	77.01	69.80	14.30	07.17
60	35.47	28.05	74.81	67.43	12.09	-
62	33.32	25.66	72.60	64.96	09.81	02.19
64	31.06	23.62	70.30	62.37	07.47	24699.55
66	28.75	20.60	67.91	59.73	-	96.84
68	26.33	17.95	65.44	57.04	02.44	94.08
70	23.89	15.19	62.88	54.27	24699.90	91.29
72	21.33	12.40	60.23	51.39	97.13	88.34
74	18.63	09.51	57.55	48.45	94.50	85.34
76	15.98	06.55	54.76	45.44	90.85	82.28
78	13.13	03.52	51.89	42.32	88.72	79.14
80	10.32	00.39	48.98	39.17	85.62	75.86
82	07.35	24397.17	45.95	35.89	82.59	72.56
84	04.31	93.11	42.88	32.54	79.42	69.05
86	01.25	90.54	39.77	29.17	76.18	
88	24398.06	87.09	36.50	25.71	72.86	
90	94.76	83.59	33.13	22.12	69.42	
92	91.38	79.99	29.69	18.49		
94	88.01	76.23	26.25	-		
96	84.53	72.47	22.70	10.95		
98	80.94	68.68	19.03			
100	77.25	64.75	-			
102	73.47		11.57			
104	69.59					
106	65.78					

Table III.2 — Wavenumbers of Rotational Lines for Te_2^{128}

J	18-0 R(J)	18-0 P(J)	20-0 R(J)	20-0 P(J)	21-0 R(J)	21-0 P(J)
14	24878.70	24876.95				
16	78.18	76.20				
18	77.60	75.40				
20	76.95	74.48				25265.50
22	76.20	73.50				64.47
24	75.40	72.46		25136.07		63.33
26	74.48	71.32		34.93	25265.28	62.13
28	73.50	70.14	25137.04	33.64	64.24	60.86
30	72.46	68.79	35.97	32.33	63.11	59.50
32	71.32	67.46	34.81	30.90	61.88	58.04
34	70.14	65.99	33.52	29.41	60.58	56.50
36	68.79	64.48	32.17	27.82	59.20	54.86
38	67.46	62.85	30.75	26.15	57.70	53.14
40	65.99	61.14	29.25	24.41	56.14	51.35
42	64.48	59.34	27.64	22.59	54.49	49.48
44	62.85	57.52	25.96	20.66	52.76	47.52
46	61.14	55.59	24.21	18.65	50.96	45.45
48	59.34	53.55	22.36	16.57	49.06	43.31
50	57.52	51.49	20.43	14.39	47.06	41.10
52	55.59	49.31	18.24	12.14	44.99	38.77
54	53.55	47.00	16.32	09.81	42.82	36.37
56	51.49	44.70	14.12	07.38	40.58	33.87
58	49.31	42.28	11.84	04.87	38.25	31.34
60	47.00	39.76	09.50	02.28	35.82	28.69
62	44.70	37.21	07.06	25099.61	33.33	25.95
64	42.28	34.54	04.54	96.84	30.74	23.13
66	39.76	31.78	01.93	94.00	28.06	20.21
68	37.21	28.92	25099.23	91.07	25.31	17.21
70	34.54	26.06	96.47	88.06	22.44	14.12
72	31.78	23.08	93.58	84.97	19.50	10.95
74	28.92	20.08	90.65	81.78	16.49	07.70
76	26.06	16.88	87.63	78.51	13.38	04.35
78	23.08	13.66	84.52	75.17	10.15	00.94
80	20.08	10.30	81.31	71.72	06.91	25197.44
82	16.88	06.89	78.02	68.20	03.52	93.79
84	13.66	03.41	74.54	64.59	00.09	90.13
86	10.30		71.20	60.89	25196.52	86.34
88	06.89		67.66	57.14	92.91	82.47
90	03.41		63.63	53.24	89.18	78.54
92			60.31	49.32	85.37	74.49
94			56.53	45.26	81.51	
96			52.61	41.16	77.46	
98			48.67	36.95	73.34	
100			44.60			
102			40.47			
104			36.21			

Table III.3 - Combination differences $\Delta_2 F''(J)$ for $v'' = 0$ of Te_2^{128}

J	15-0	16-0	17-0	18-0	20-0	21-0	Average
15	2.51	2.45	2.45	2.50			2.48
17	2.77	2.76	2.77	2.78			2.77
19	3.13	3.05	3.08	3.12			3.10
21	3.43	3.65	3.39	3.45			3.42
23	3.74	3.84	3.74	3.74			3.77
25	4.08	4.11	4.03	4.08			4.08
27	4.37	4.44	4.44	4.34		4.42	4.40
29	4.69	4.52	4.76	4.70	4.71	4.74	4.72
31	5.02	5.14	5.06	5.00	5.07	5.07	5.06
33	5.32	5.44	5.39	5.32	5.40	5.38	5.38
35	5.58	5.74	5.70	5.66	5.70	5.72	5.70
37	5.93	6.03	6.05	5.94	6.02	6.06	6.01
39	6.27	6.29	6.36	6.32	6.34	6.35	6.32
41	6.59	6.61	6.67	6.65	6.66	6.66	6.64
43	6.92	7.00	7.02	6.96	6.98	6.97	6.98
45	7.24	7.39	7.34	7.26	7.31	7.31	7.32
47	7.55	7.69	7.64	7.59	7.64	7.65	7.64
49	7.87	7.96	7.97	7.85	7.95	7.96	7.93
51	8.17	8.25	8.29	8.21	8.29	8.29	8.25
53	8.52	8.61	8.62	8.59	8.43	8.62	8.66
55	8.83	8.93	8.93	8.85	8.94	8.95	8.91
57	9.17	9.27	9.25	9.21	9.25	9.24	9.23
59	9.51	9.58	-	9.55	9.56	9.56	9.55
61	9.81	9.85	9.90	9.79	9.89	9.87	9.85
63	10.16	10.23	10.25	10.16	10.22	10.20	10.20
65	10.46	10.57	10.62	10.50	10.54	10.53	10.54
67	10.80	10.87	-	10.84	10.86	10.85	10.84
69	11.13	11.17	11.15	11.15	11.17	11.19	11.16
71	11.49	11.47	11.55	11.46	11.50	11.49	11.49
73	11.82	11.78	11.79	11.70	11.80	11.80	11.78
75	12.08	12.11	12.12	12.04	12.14	12.14	12.11
77	12.46	12.44	12.71	12.40	12.46	12.44	12.44
79	12.74	12.72	12.86	12.78	12.80	12.71	12.77
81	13.15	13.09	13.06	13.19	13.11	13.12	13.12
83.	13.44	13.41	13.53	13.47	13.43	13.39	13.41
85	13.77	13.71			13.65	13.75	13.72
87	14.16	14.06			14.06	14.05	14.08
89	14.47	14.38			14.42	14.37	14.41
91	14.77	14.64			14.31	14.69	14.70
93	15.15	-			15.06		15.11
95		15.30			15.37		15.34
97					15.66		15.66

Table III.4(a) - Wavenumbers of Rotational Lines for Te_2^{128}

	19-0	
J	R(J)	P(J)
112		24878.53
114		73.71
116		68.79
118	24877.85	63.78
120	73.02	58.68
122	68.11	53.55
124	63.11	48.39
126	58.01	42.99
128	52.87	37.58
130	47.61	32.09
132	42.28	26.54
134	36.89	20.89
136	31.37	
138	25.76	
140	20.08	

Table III.4(b) - Combination differences $\Delta_2 F''(J)$ for Te_2^{128}

J	R(J-1) - P(J+1)
119	19.17
121	19.47
123	19.81
125	20.11
127	20.43
129	20.78
131	21.07
133	21.39

Table III.5(a) – Band origin values for Te_2^{128}

v'–v"	ν_o in cm^{-1}	$-(B_v' - B_v'')$ in cm^{-1}
15–0	24465.72	0.0094
16–0	24606.22	0.0096
17–0	24744.22	0.0098
18–0	24879.74	0.0100
19–0	25018.50	0.0101
20–0	25143.97	0.0104
21–0	25271.48	0.0107

Table III.5(b)–Rotational constants for Te_2^{128}

B_{15}'	0.0308 cm^{-1}	B_e'	0.0339 cm^{-1}
B_{16}'	0.0306 "	r_e'	2.785Å
B_{17}'	0.0304 "	α_e'	0.0002 cm^{-1}
B_{18}'	0.0302 "	D_e'	$\sim 10^{-8}$ cm^{-1}
B_{19}'	0.0300 "	B_0''	0.0402 cm^{-1}
B_{20}'	0.0298 "	r_0''	2.558Å
B_{21}'	0.0295 "		

Table III.6(a)-Isotopic shifts from band origin data

$v''-v'''$	ν_o in cm^{-1} Te$_2^{128}$	ν_o in cm^{-1} for Te$_2^{130}$ acc. to Jha	$\Delta\nu_o$
15-0	24465.72	24450.09	15.63
16-0	24606.22	24589.34	16.88
17-0	24744.22	24726.44	17.78
18-0	24879.74	24861.54	18.20
19-0	25018.50	24996.30	22.20
20-0	25143.97	25124.04	19.93
21-0	25271.48	25251.04	20.44

Table III.6(b)-Comparison of the rotational constants (in cm^{-1}) for Te$_2^{128}$ and Te$_2^{128}$(Cal.)

	B_e'	α_e'	B_o''
Te$_2^{128}$	0.0339	0.0002	0.0402
Te$_2^{128}$ (Calculated from Te$_2^{130}$ data)	0.0340	0.0002	0.0402
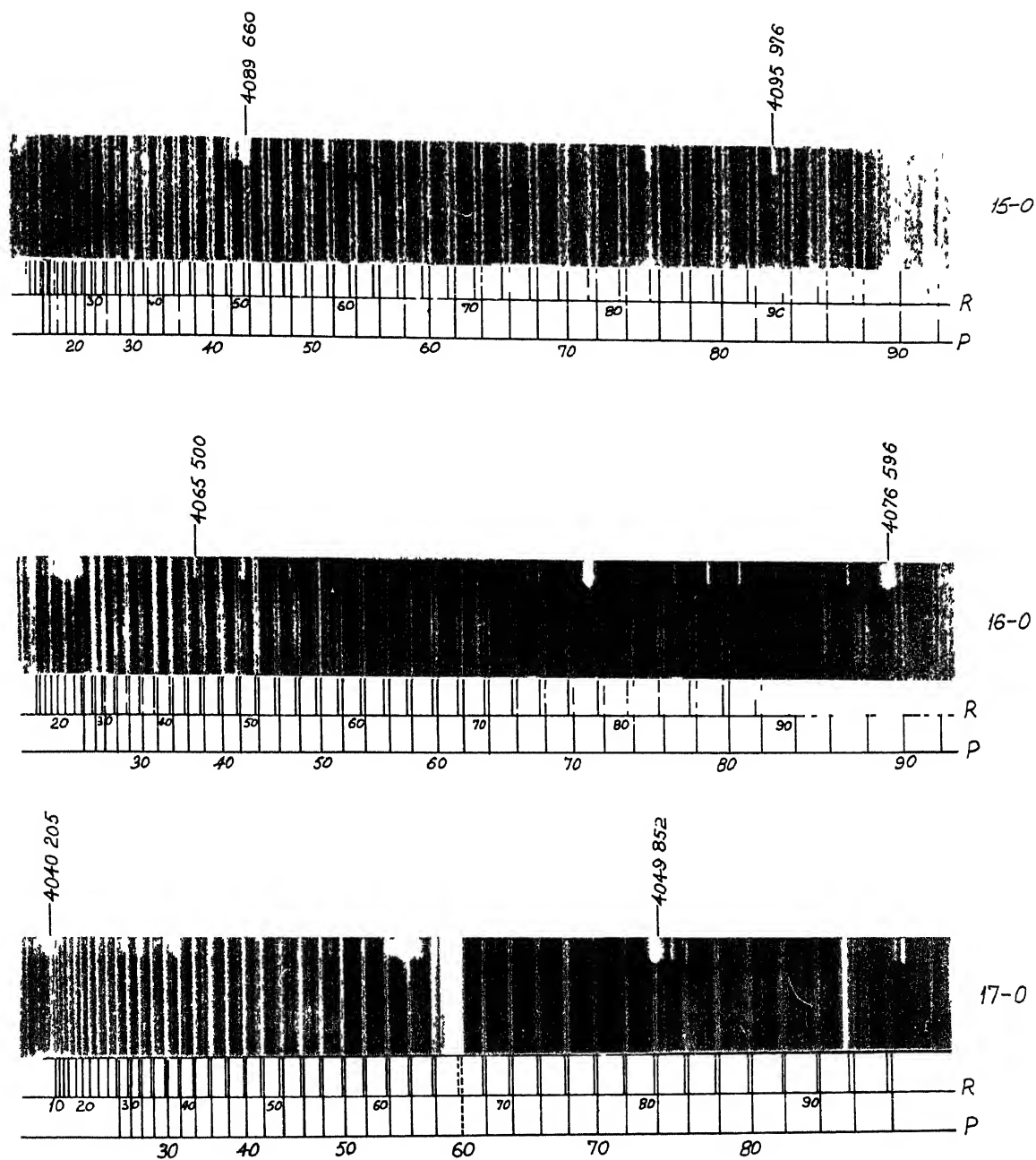
Fig III 1 Rotational Structure of 15-0,16-0,17-0 bands of Te_2^{128} photographed in the II order of Jarrell-Ash grating Spectrograph at a dispersion of 0 6 Å/mm
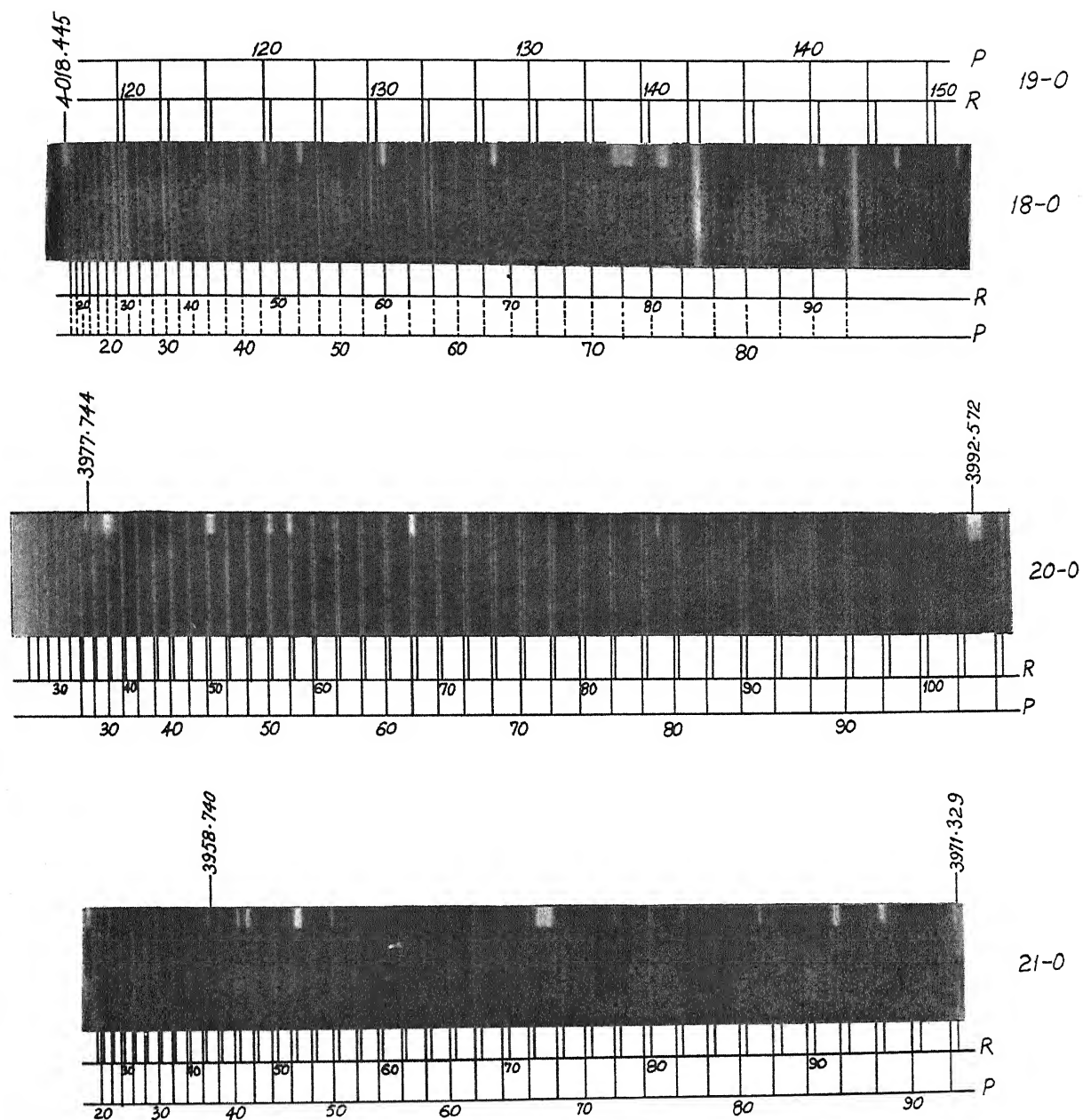
Fig. III·2: Rotational Structure of 18-0, 19-0, 20-0, 21-0 bands of Te_2^{128} photographed in the III order of a Jarrell-Ash grating spectrograph at a dispersion of 0.6 Å/mm.
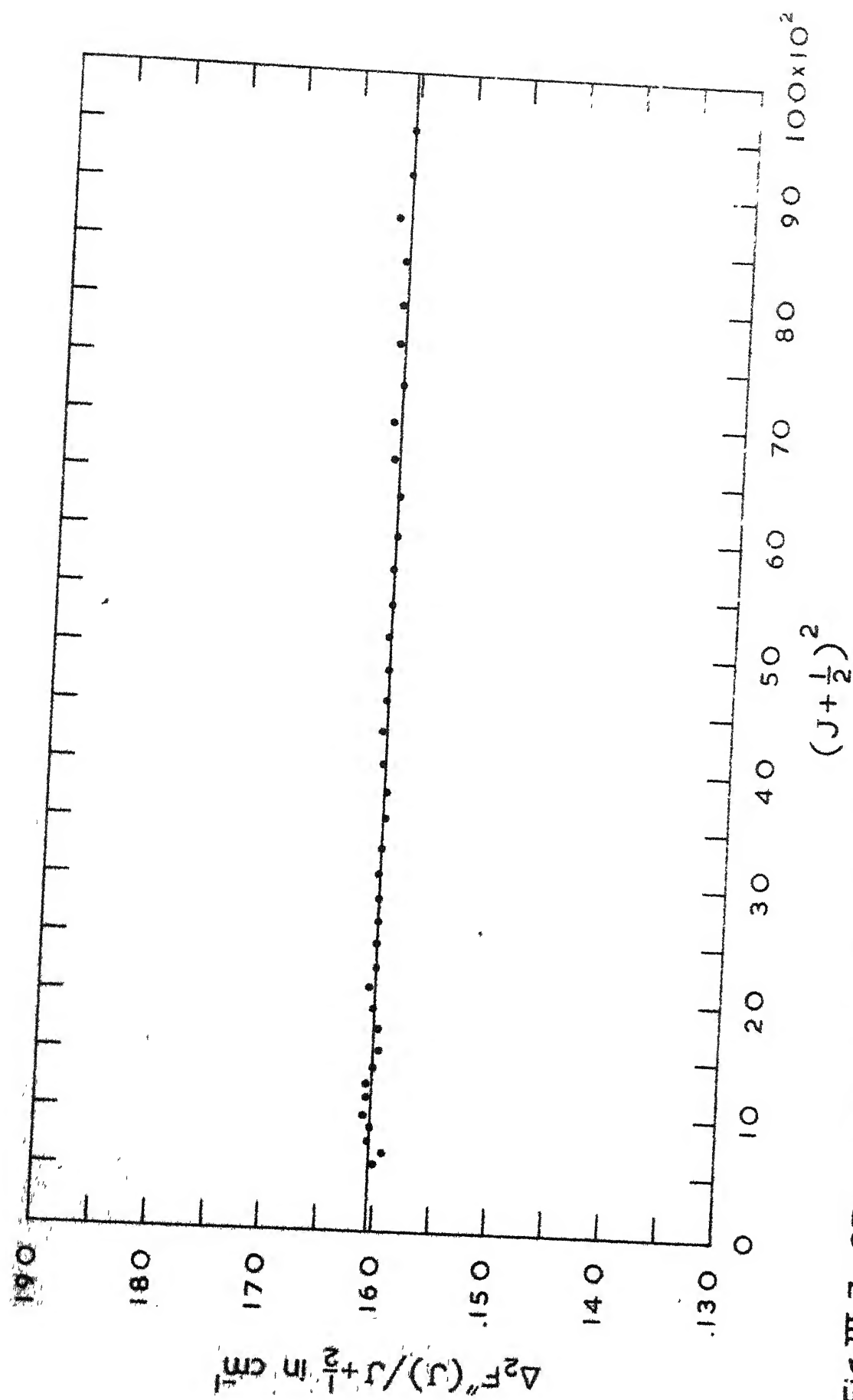
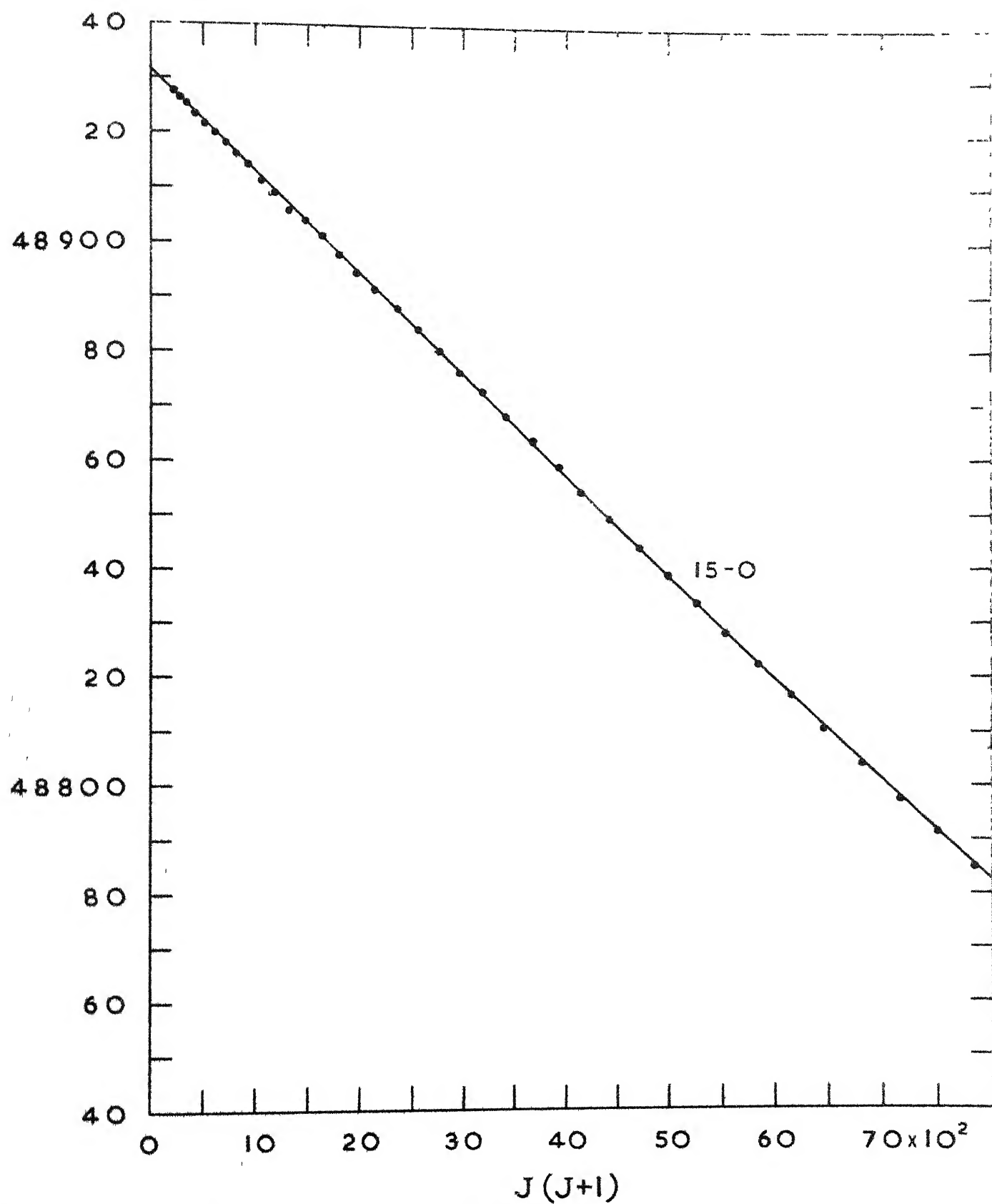Fig. III.3 – GRAPHICAL DETERMINATION OF ROTATIONAL CONSTANTS AND CHECKING OF J NUMBERING for $v''=0$ of Te_2^{128}
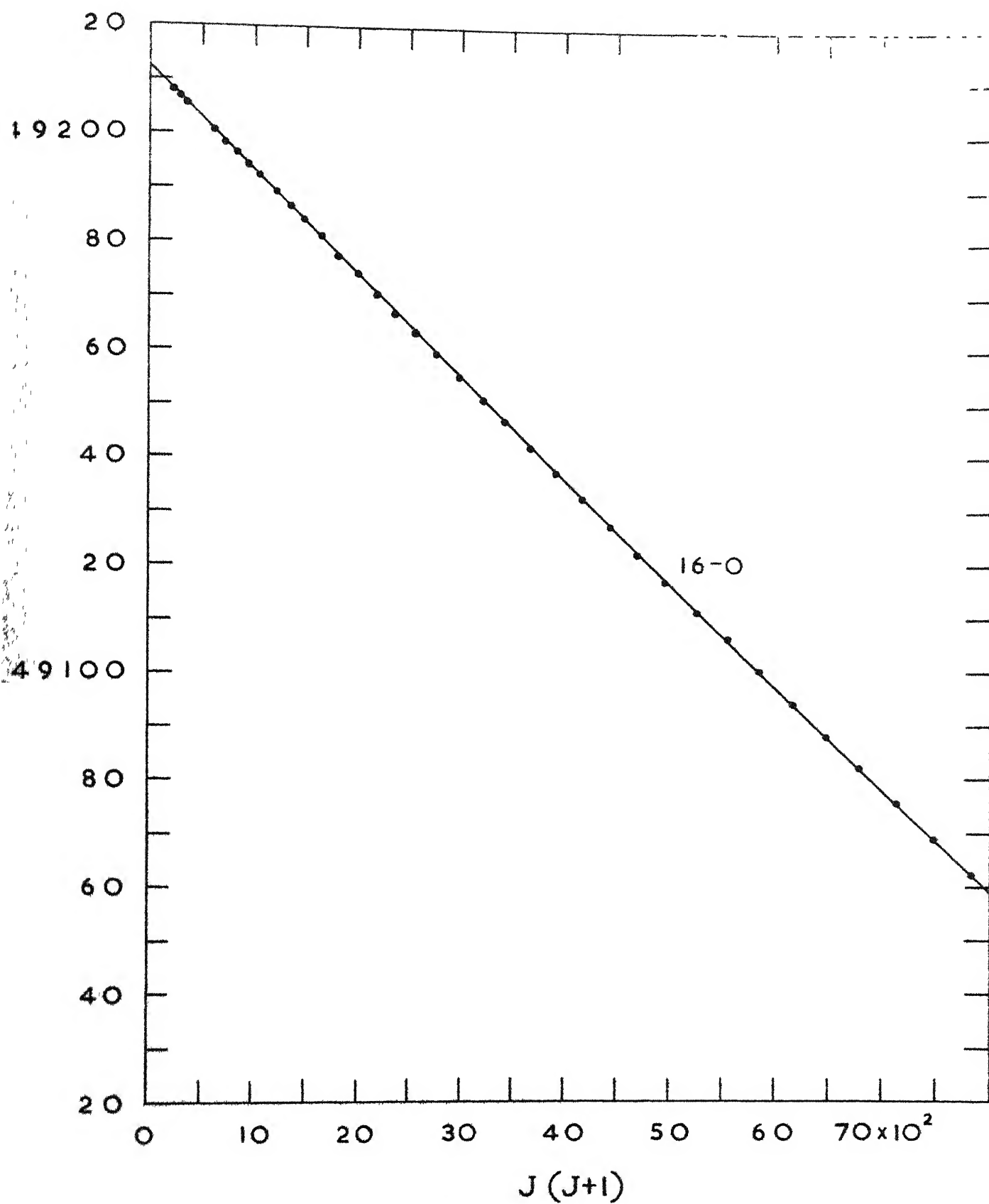
Fig. III 4 (a) - GRAPHICAL DETERMINATION OF THE BAND ORIGIN

$J (J+1)$

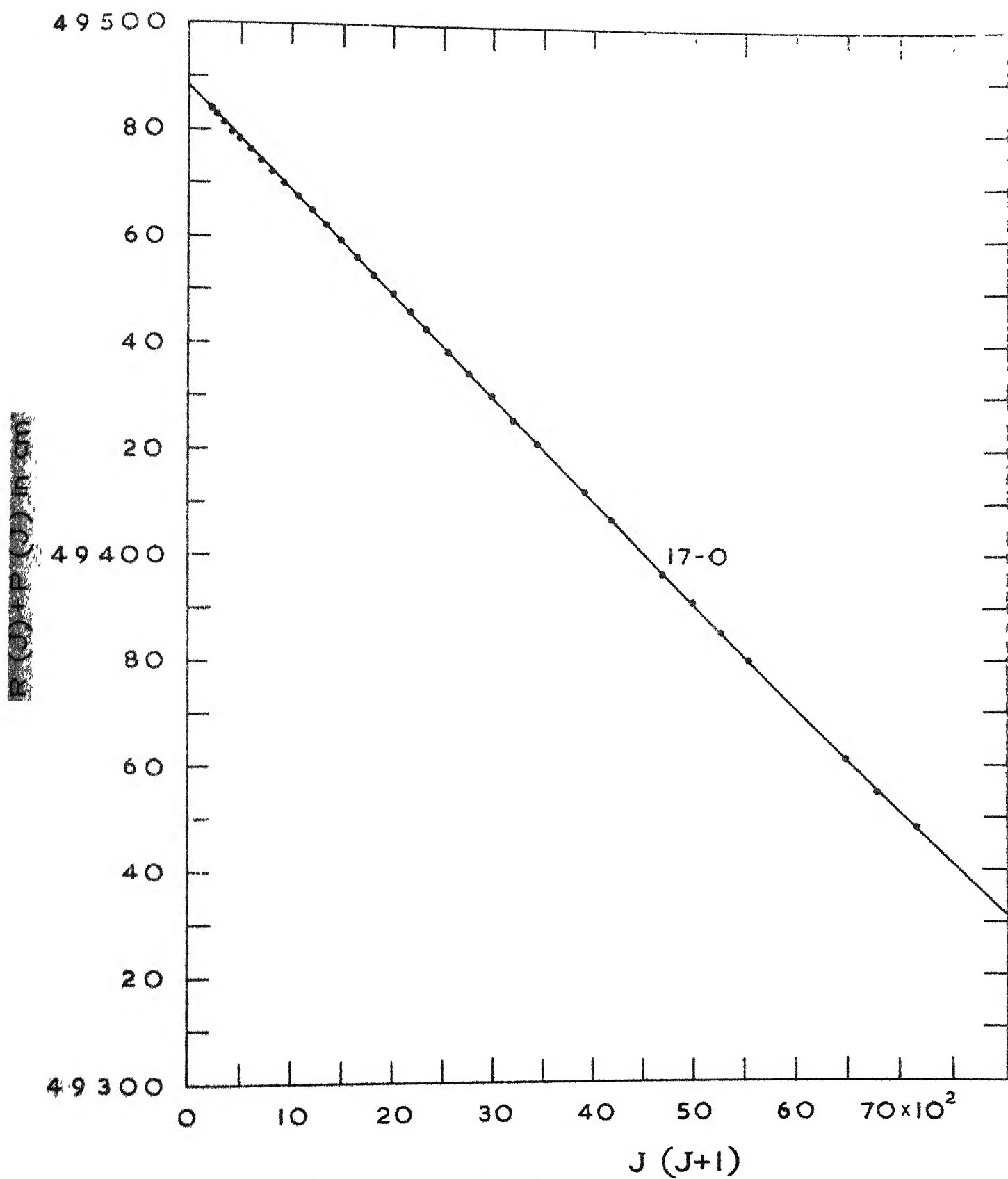III 4 (b) - GRAPHICAL DETERMINATION OF THE BAND ORIGIN
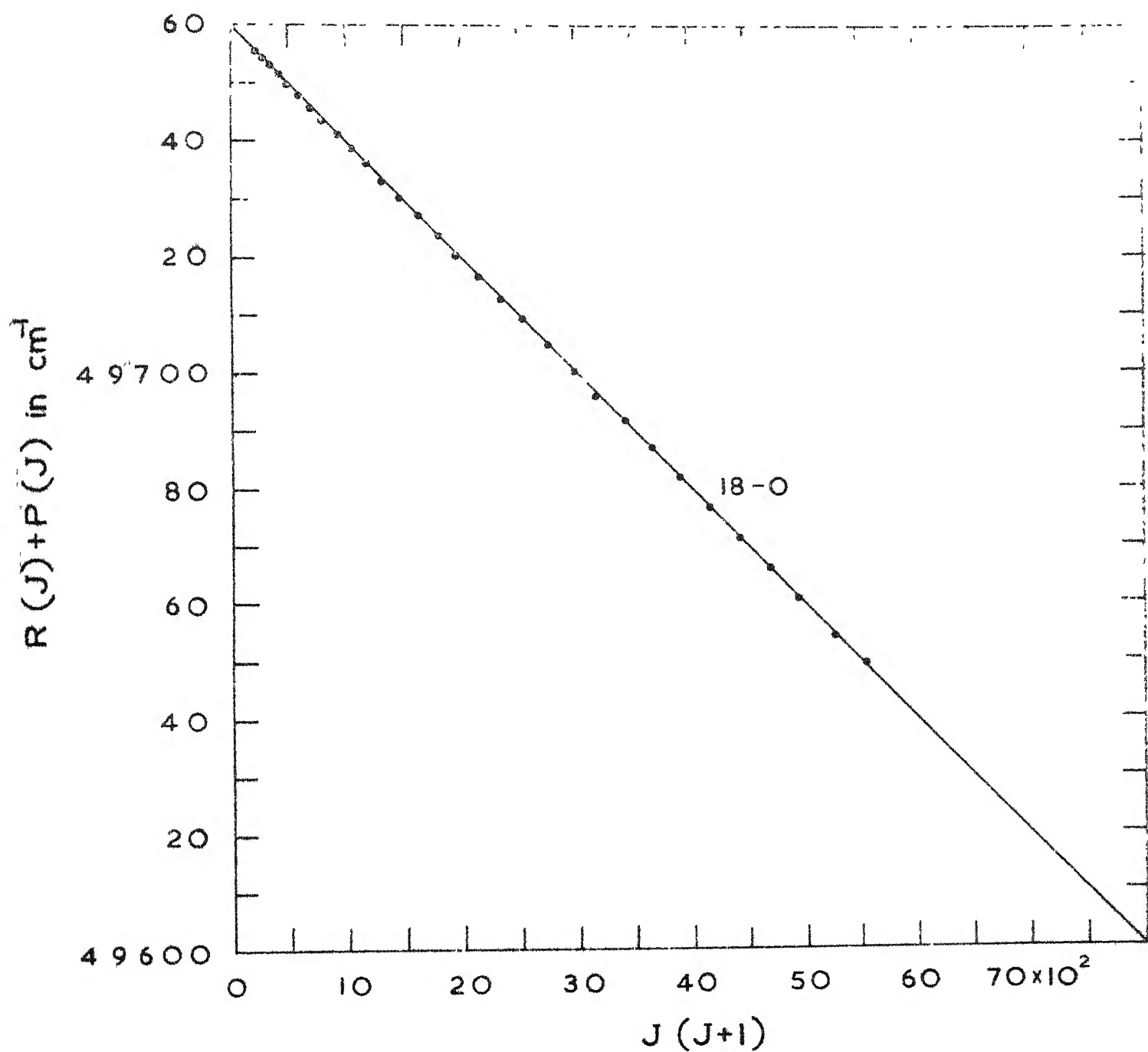
Fig.III.4(c)-GRAPHICAL DETERMINATION OF THE BAND ORIGIN

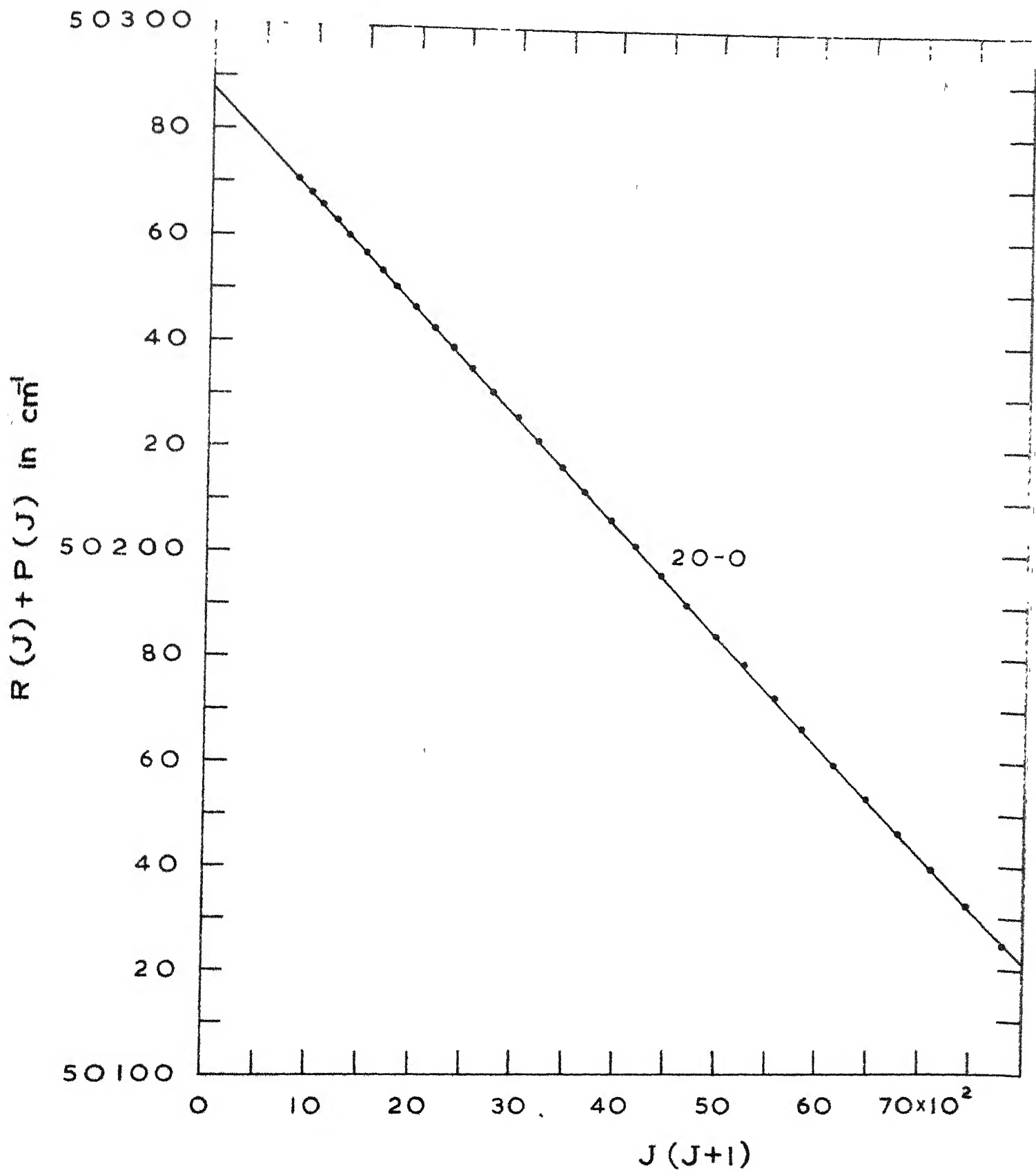Fig.III.4 (d) - GRAPHICAL DETERMINATION OF THE BAND ORIGIN

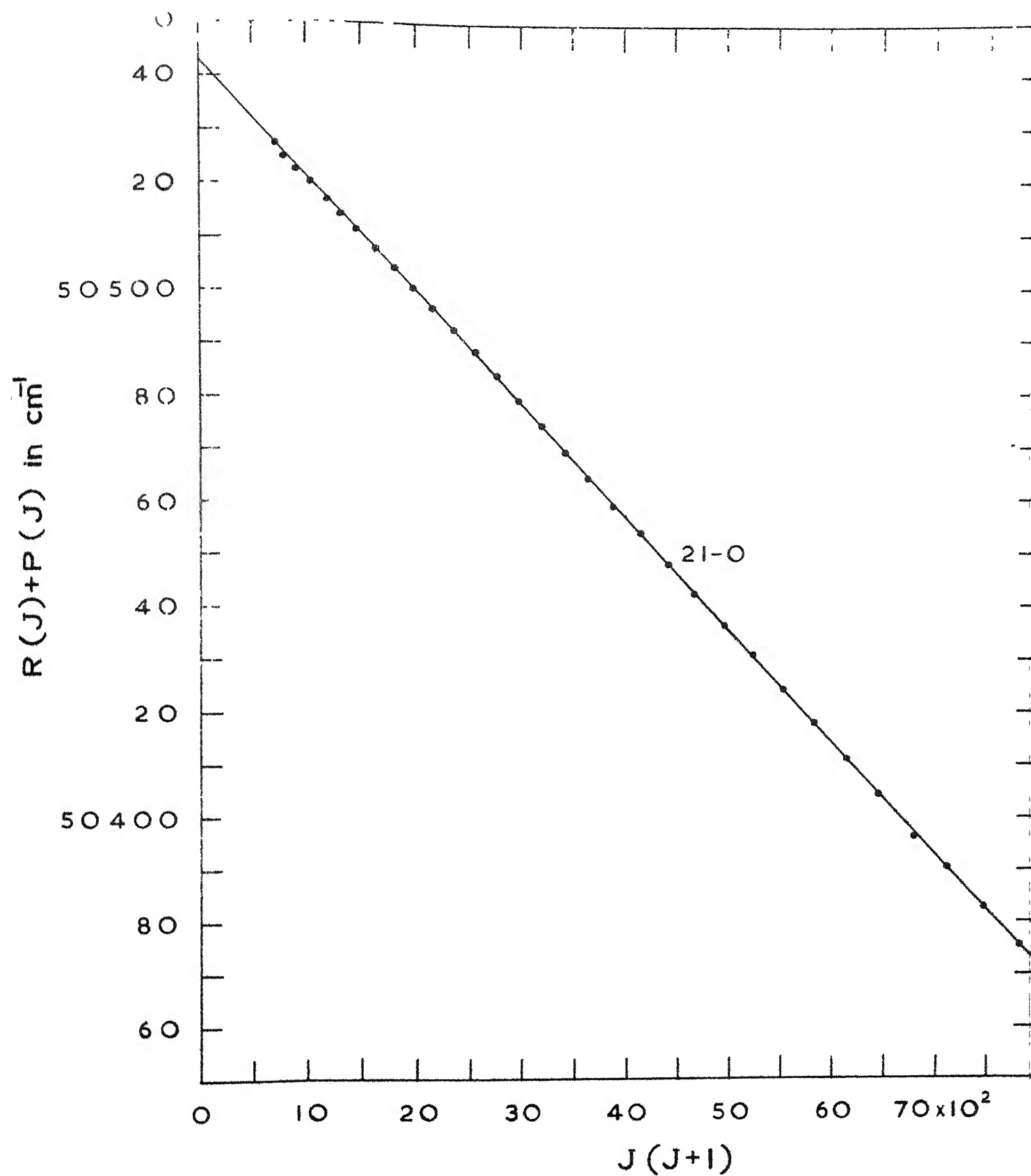Fig.III.4(e) GRAPHICAL DETERMINATION OF THE BAND ORIGIN

Fig.III.4(f)-GRAPHICAL DETERMINATION OF THE BAND ORIGIN

CHAPTER IV

THE A $^2\Pi$ - X $^2\Sigma$ SYSTEM OF CaF

ABSTRACT

The $A^2 \pi - X^2 \Sigma$ system of CaF which lies in the region $6300\overset{\circ}{A} - 5830\overset{\circ}{A}$ is reinvestigated by exciting the CaF_2 sample in a 150 V D.C. carbon arc at 6-12A current. More members were observed in some of the known sequences. Some comments are offered on the $\triangle v = +1$ sequence.

INTRODUCTION

A number of workers have studied the emission and absorption spectra of halides of II group elements in detail. In particular, the fluorides have been extensively worked out. Datta (1921) was the first worker to carry out investigations on MgF, CaF, SrF and BaF molecules, in emission from a carbon arc. Johnson (1929) continued his investigations on these molecules to give a quantum picture to the spectra.

It was suggested by Mulliken (1931) that the first excited state is $^2\pi$ in all the II group fluorides, ~~It is~~ and ~~found~~ that it is an inverted state in BeF.
More involved calculations were done by Walker and Richards(1967) by taking the configuration interaction into account which prove Mulliken's (1931) suggestion. The next molecule MgF belonging to the same group was proved to have an inverted state as the first excited state by Barrow and Beale (1967). It was also shown that in BaF, $A^2\pi$ is a regular state by Barrow and others (1967). However, no such information regarding the first excited state of CaF molecule was available either experimentally or with the help of any calculations. The high resolution work carried out by Mohanty and Upadhya (1967) on the (0,0) band in both the sub-systems of CaF, A-X system assumed that the first excited state is regular. It was felt that an experimental study of this system involving the first excited state and the ground state might reveal about the nature of the excited state more explicitly. The known

absorption bands in the ultra-violet region by Fowler (1941) have not been observed in emission so far. It was thought worthwhile to try various experimental conditions for observing emission spectra of the ultra-violet systems. The details of these investigations and the results obtained thereby are discussed in this Chapter.

EXPERIMENTAL

CaF_2 salt was burnt in a carbon arc at 150 V D.C. and at 6 - 12A current and the resulting spectra were photographed on a 3.4 meter Jaco grating spectrograph. While no new emission systems were obtained even at the highest currents used, it was found that extra bands were observed in some of the known sequences of the $A^2 \pi - X^2 \Sigma$ system of CaF. For clarity, the $\triangle$ v=0 and -1 sequences were photographed in the Ist order of a grating (30,000lpi) blazed for 4,000Å at a dispersion of 2.4Å/mm. It was found necessary to photograph the $\triangle$ v= +1 sequence in the II order of grating (30,000 lpi) blazed for 10,000Å at a dispersion of about 1.0Å/mm. At this stage it was observed that the structure of the bands is overlapped by the neighbouring ones and it was not possible to do rotational analysis with the available resolution in this laboratory. The exposure timings were varied from 2 to 4 minutes to record the spectra on Ilford R-40 plates. Iron arc was used as standard. The measurements of the band heads were done on a Zeiss Abbe comparator and the accuracy of the measurements was found to be about $\pm 0.5 cm^{-1}$. All the calculations of the band head measurements were done on an IBM computer.

RESULTS AND DISCUSSION

$A^2 \pi_{3/2} - X^2 \Sigma$ sub-system: In the $\Delta v = -1$ sequence, eight bands belonging to P_2 series were observed out of which none were reported by earlier workers and Q_2 series consist of four new bands. However, $\Delta v = +1$ sequence shows only Q_2 heads and appears as if it has originated at 5830Å and starts diverging towards longer wavelength side and all the band heads appear to be degraded to violet. These features are marked in Fig. IV.1(c). Johnson's (1929) assignment starts from (4,3) and the band head lies at 17145.6 cm^{-1}. This numbering was thought to be uncertain by Harvey (1931), who was the first worker to estimate the rotational constants of CaF molecule, since it was not resolved properly and the first few Q_2 heads were supposed to be superposed. In the present work this portion of the spectrum is clearly resolved and it shows that the bands actually start from 17146.1cm^{-1} and this is taken at (1,0) band of this sequence and subsequently 17145.6cm^{-1} becomes the (2,1) band and so on upto (17,16). The band heads do exist beyond this but indeed they are too weak to be measured. This goes in to show that there is no sudden dis-appearance of the bands after (17,16) contradicting the observation of Johnson(1929) about the dissociation of the CaF molecule.

$A^2 \pi_{1/2} - X^2 \Sigma$ sub-system: The Q_{12} series in $\Delta v = -1$ sequence has two more band heads than observed by previous workers and P_{12} series consist of six bands starting from 15865.6cm^{-1} as observed

by Harvey (1931). He argued since it is the first band to be recorded in this sequence, it should be the (0,1) band head and that Johnson's (1929) numbering should be lowered by at least two units. However, this suggestion brings in a difficulty in identifying the difference between the Q_{12} and P_{12} heads in this sequence, in concurrence with all other sequences observed, unless one assumes some sort of perturbation to all the P_{12} heads. This assumption should bring in the same descrepancy in the corresponding Q_{12} heads also, because there are common levels whereto the transitions are observed. But since no such descrepancy exists in the Q_{12} heads, Johnson's (1929) numbering is preserved and no obvious explanation is at sight for the first two missing heads except that they might exist and are very weak to be recorded.

A set of very weak and red degraded bands were recorded beyond the $\triangle v = +1$ sequence of $^2\pi_{3/2} - {}^2\Sigma$ sub-system. The band heads are 17057.1, 49.0, 40.4, 31.4, 22.8, 13.6, 04.7, and $16995.2cm^{-1}$ out of which the first two heads were not observed by Harvey (1931) though he observed some heads still to the lower frequency side where there is a heavy overlapping by the intense Na doublet. It is quite possible that they may belong to the Q_2 series with very high numbering which only can give the reversal of shading because of the change in the sign of $(B_v' - B_v'')$ as Harvey (1931) suggested. However, it is interesting to note that the microphotometer trace of Harvey's (1931) emission spectrum plate showed a diffuse maximum with its centre at $17076.6cm^{-1}$ (5853.7Å). He argued from the intensity

considerations that this might correspond to the integrated effect of the Q_2 heads in $\triangle v = +1$ sequence of this sub-system, though no heads of any strength are visible. In the present work, a moderately intense line was observed at the same wavelength and it was identified as an atomic line due to Ba (5853.679$\overset{o}{A}$) which generally appears in Ca salts as an impurity. That this line belongs to Ba is confirmed by the presence of other Ba atomic line on the plate quite closeby (5826.295$\overset{o}{A}$). The presence of impurity lines due to Barium was further checked from the identified line at 6141.72$\overset{o}{A}$. Thus the existence of Q_2 heads of $\triangle v = +1$ sequence of this sub-system is still not certain.

All the observed band heads were fed to a least squares fit programme and formulae governing the series were derived. From the formulae obtained for Q_{12} and Q_2 heads in $\triangle v = 0$ and -1 sequences in both the sub-systems, the vibrational constants were derived and they were found to be in close agreement to the already existing values for the ground state and the excited state.

The wavenumbers of all the band heads are given in Table IV.1 with the newly observed bands duly marked.

However, with the help of the rotational constants and band origin data given by Mohanty and Upadhya(1967) for the (0-0) band in both the sub-systems, the Q_{12} branch and Q_2 branch were generated and it was found that the corresponding band heads should lie at 16487.3cm^{-1} and 16562.2cm^{-1} respectively whereas the observed band heads are at 16484.9cm^{-1} and 16560.1cm^{-1}. The cause for this large difference between the observed and generated values is not obvious.

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Table IV.1 - Experimental Data and Vibrational Analysis of A - X System of CaF

$^2\Pi_{3/2} - {}^2\Sigma$ Sub-System

$\Delta v=-1$			$\Delta v=0$		$\Delta v=+1$		
Q_2	(v',v'')	P_2	O_2	(v',v'')	P_2	O_2	(v',v'')
15978.6	(0,1)		16560.1	(0,0)	16522.0	*17146.1	(1,0)
89.9	(1,2)	*15951.6	65.7	(1,1)	27.5	45.6	(2,1)
16001.0	(2,3)	*63.0	71.2	(2,2)	32.7	44.7	(3,2)
11.5	(3,4)	*74.0	76.0	(3,3)	37.0	43.5	(4,3)
21.6	(4,5)	*84.6	80.7	(4,4)	41.6	42.0	(5,4)
31.5	(5,6)	*95.1	84.9	(5,5)	45.5	40.1	(6,5)
40.9	(6,7)	*16004.3	88.3	(6,6)	49.0	38.0	(7,6)
*50.0	(7,8)	*13.0	91.6	(7,7)		35.4	(8,7)
56.7	(8,9)	*21.8	94.9	(8,8)		32.6	(9,8)
67.2	(9,10)					29.4	(10,9)
*75.1	(10,11)					25.8	(11,10)
*82.7	(11,12)					21.9	(12,11)
*90.2	(12,13)					17.5	(13,12)
						12.7	(14,13)
						07.4	(15,14)
						01.8	(16,15)
						17095.2	(17,16)

$^2\Pi_{1/2} - {}^2\Sigma$ Sub-System

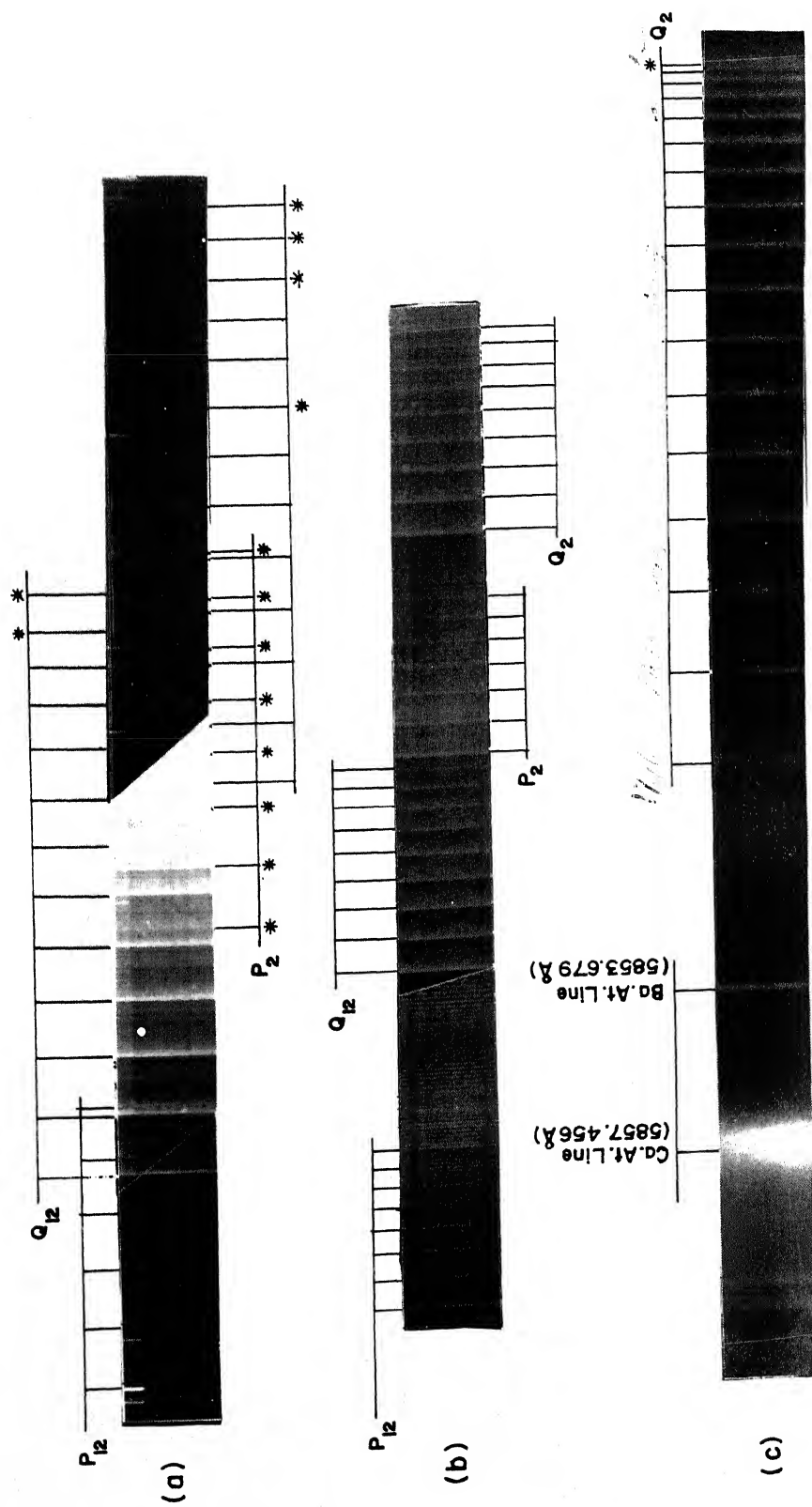| $\Delta v=-1$			$\Delta v=0$		$\Delta v=+1$
Q_{12}	(v',v'')	P_{12}	Q_{12}	(v',v'')	P_{12}
15905.5	(0,1)		16484.9 / *64.8	(0,0)	16424.0
16.8	(1,2)		90.6	(1,1)	29.2
27.8	(2,3)	15865.6	95.8	(2,2)	34.0
38.4	(3,4)	77.0	16500.6	(3,3)	38.5
48.5	(4,5)	87.9	05.2	(4,4)	42.1
58.2	(5,6)	98.4	09.2	(5,5)	46.0
67.7	(6,7)	15908.7	13.2	(6,6)	50.1
76.6	(7,8)	18.3	16.4	(7,7)	53.9
85.1	(8,9)		19.7	(8,8)	
94.9	(9,10)				
16001.0	(10,11)				
*08.5	(11,12)				
*15.9	(12,13)				

*Bands observed in the present investigation

FIG. IV.I - Photograph showing $\Delta V = -1,0$ and $+1$ sequences respectively of $A^2\pi - X^2\Sigma$ system of CaF Newly observed bands are marked $*$.

VITAE

The author was born on 5th June 1942 in the State of
Andhra Pradesh. He obtained his B.Sc. degree and M.Sc. degree in
Physics-Spectroscopy from Banaras Hindu University in 1960 and
1962 respectively. Since then he has been working in the Departme
of Physics, Indian Institute of Technology, Kanpur.

PHY-1969- D - SUB-ISO